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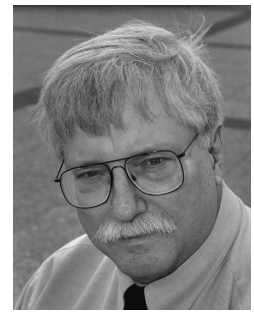
The U.S. Environmental Protection Agency's Particulate Matter Supersites Program: An Integrated Synthesis of Scientific Findings and Policy- and Health-Relevant Insights

By Guest Editors Paul A. Solomon and Philip K. Hopke



The U.S. Congress and the National Research Council in their 1998 report "Research Priorities for Airborne Particulate Matter," identified the need to better characterize the spatial and temporal composition of particulate matter (PM) in ambient air that potentially have adverse human health and welfare effects. Given this direction, the U.S. Environmental Protection Agency (EPA) developed what is now commonly referred to as the PM Supersites Program. The Supersites Program consisted of eight regional studies with central sites in New York City, NY; Pittsburgh, PA; Baltimore, MD; Atlanta, GA; St. Louis, MO; Houston, TX; Fresno, CA; and Los Angeles, CA. Significant collaboration occurred with other research studies and established national air quality and meteorological monitoring networks resulting in a truly a coast-to-coast national program. Over 400 peer-reviewed journal articles have thus far resulted from the program; others continue to be published. An international specialty conference (AAAR, February, Atlanta, GA, 2005; www.aaar.org/index2.cfm?section=Meetings_and_Events&content=Archived_Meetings; scroll down to Supersites Conference) and nine special journal issues dedicated to Supersites Program results have been published, including a series of 10 technical synthesis papers in the February 2008 issue of the *Journal of the Air & Waste Management Association* addressing 16 science-policy relevant questions identified by EPA in conjunction with its public and private sector partners. An archival database is available from NARSTO (eosweb.larc.nasa.gov/PRODOCS/narsto/table_narsto.html), and a relational database is available at the Georgia Institute of Technology (http://sird.ce.gatech.edu).

This dedicated special issue of the *Journal of the Air & Waste Management Association* contains a single peer-reviewed paper providing an integrated synthesis of results from the Supersites Program and related studies. It provides a technical summary of the program from 1999 through early 2008. Interpreted from the key atmospheric sciences findings are important policy-relevant insights for use by public and private sector organizations whose goal it is to efficiently and cost effectively reduce risk from PM and other pollutants. Also interpreted from the atmospheric sciences findings are health-relevant insights to provide guidance for future health and exposure scientists who are planning studies to understand the adverse impacts of PM on human health. The conclusion section of the paper includes the policy- and health-relevant insights along with identification of selected knowledge gaps to guide future research. A series of detailed tables organize the great expanse of information from the Program along specific topic areas. Finally, a nearly comprehensive bibliography through early 2008 provides details supporting presented results. This paper, therefore, provides a useful reference to those interested in finding additional details of the significant scientific advances in PM method and in understanding the accumulation of PM on urban and regional scales and related policy- and health-relevant insights, as achieved through the Supersites Program and related studies.

A few of the many policy- and health-relevant insights derived through this integrated synthesis are summarized below. No implication is given to the importance of the order listed here or to the importance relative to the others listed within the integrated synthesis.

The major chemical components of fine PM ($PM_{2.5}$; particles <2.5 μm in aerodynamic diameter) and their spatial and temporal variations have not changed significantly during the last decade driven by similarities over time in source emissions and meteorology. The Supersites Program clearly identified the importance of secondary PM, especially secondary organic aerosol (SOA), a significant fraction of which comes from biogenic precursor species even in urban areas. Secondary PM (sulfate, nitrate, and SOA) often drives seasonal variations in $PM_{2.5}$. Regional PM related pollution is often superimposed on urban primary emissions and locally formed secondary PM resulting in higher concentrations in urban than rural areas. In combination, the spatial and temporal variability due to different source mixes and meteorology either on local or regional scales implies the potential need for different emissions control strategies by region of the country and season. The regional nature of PM will require regional as well as local emissions controls.

The detailed composition of organic aerosols and estimates of SOA, although advanced considerably during the last 8 yr, are still highly uncertain. As advances continue to occur, uncertainty in apportioning PM at receptors to sources will be reduced.

New continuous methods were developed and evaluated and existing methods evaluated during the Supersites Program; including methods for measuring ultrafine (UF) mass, coarse mass, chemical components (e.g., ions, organic carbon, elemental carbon), particle-bound water (PBW), particle density, and the composition of singe particles and of particle size distributions. The latter by particle mass spectrometers, which likely represent the most significant advancement in PM measurement methods technology in the past decade. The tapered element oscillating microbalance operated with a filter dynamics measurement system (FDMS-TEOM) appears to provide the best estimate of $PM_{2.5}$ mass relative to that found in air, and does so at a time resolution of 1 hr or less.

Applications of continuous methods provide significant additional information on the spatial and temporal distribution of PM and its components, allowing new insights into atmospheric processes, source-receptor relationships, and emissions-based model evaluation. Use of continuous methods plainly showed the considerable variability in PM and its components and the great loss of information, including spatial variability, when only 24-hr measurements are available.

Significant advances in understanding UF particle formation, composition, spatial and temporal distributions, and growth to larger particle sizes were achieved in multiple locations and over all seasons. Particle mass spectrometers played a major role in achieving these advances. Spatial scales examined ranged from UF PM near roadways (within 300 m) showing the complex nature of growth and volatilization within this short distance to regional nucleation bursts where high concentrations of initially acidic UF particles occurred over distances of hundreds of kilometers nearly simultaneously (e.g., Pittsburgh and Philadelphia). People living near freeways (within 300 m) are exposed to a different aerosol than those living only 300 m away because of variations in UF PM over the short distance, and this variation is not detected in measurements of $PM_{2.5}$, even if obtained at high time resolution.

Significant advances were seen in tools used to estimate source contributions at a receptor site via receptor modeling. These new tools in conjunction with continuous methods and inclusion of other variables, such as meteorology, provide reduced uncertainty in source apportionment estimates. The most advanced tools, using hybrid receptor and Gaussian plume models, can provide specific source information, including emissions estimates of specific PM components, rather then just source type impacts.

PBW was measured directly for the first time on an hourly basis across the full size distribution from a few nanometers to 10 μm. PBW can comprise a significant fraction of PM mass. In the eastern United States, PBW only appears to be important during the summer and is associated with acidic aerosols. Particles in the summer (acidic) appear to retain water below the equilibration relative humidity (RH) currently required for weighing Federal Reference Method compliance filters, suggesting a lower RH might be required if dry mass is desired for the $PM_{2.5}$ reference method. Wet, acidic particles also may provide an easier mechanism for dissolution of trace elements while in the air, and thus, the more rapid transfer to lung fluids of already dissolved potentially toxic PM components.

Finally, we would like to thank all those who contributed to the formation of this integrated synthesis and the Supersites Program in general. The list of contributors is extensive and includes Supersites Program principal investigators, their students and staff; those who directly collaborated with the Supersites Program, especially during the three intensive monitoring programs resulting in the Eastern Supersites Program; and those in EPA's Office of Air Quality Planning and Standards and Office of Research and Development who funded the Supersites Program directly as well as related studies. EPA through its Office of Research and Development partially funded and collaborated in the preparation of this synthesis. This manuscript has been subjected to EPA review and approved for publication. Mention of trade names or commercial products does not constitute endorsement, certification, or recommendation for use.

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Key Scientific Findings and Policy- and Health-Relevant Insights from the U.S. Environmental Protection Agency's Particulate Matter Supersites Program and Related Studies: An Integration and Synthesis of Results

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ABSTRACT

In 1998, the U.S. Environmental Protection Agency (EPA) initiated a major air quality program known as the Particulate Matter (PM) Supersites Program. The Supersites Program was a multiyear, $27 million air quality monitoring program consisting of eight regional air quality projects located throughout the United States, each with differing atmospheric pollution conditions resulting from variations in source emissions and meteorology. The overall goal of the program was to elucidate source-receptor relationships and atmospheric processes leading to PM accumulation on urban and regional scales; thus providing the scientific underpinning for modeling and data analysis efforts to support State Implementation Plans and more effective risk management approaches for PM. The program had three main objectives: (1) conduct methods development and evaluation, (2) characterize ambient PM, and (3) support health effects and exposure research. This paper provides a synthesis of key scientific findings from the Supersites Program and related studies. EPA developed 16 science/policy-relevant questions in conjunction with state and other federal agencies, Regional Planning Organizations, and the private sector. These questions were addressed to the extent possible, even given the vast amount of new information available from the Supersites Program, in a series of papers published as a special issue of the *Journal of Air & Waste Management Association* (February 2008).

This synthesis also includes discussions of: (1) initial Supersites Program support for air quality management efforts in specific locations throughout the United States; (2) selected policy-relevant insights, based on atmospheric sciences findings, useful to air quality managers and decision makers planning emissions management strategies to address current and future PM National Ambient Air Quality Standards (NAAQS) and network planning and implementation; (3) selected health-relevant insights interpreted from atmospheric sciences findings in light of future directions for health and exposure scientists planning studies of the effects of PM on human health; and (4) selected knowledge gaps to guide future research. Finally, given the scope and depth of research and findings from the Supersites Program, this paper provides a reference source so readers can glean a general understanding of the overall research conducted and its policy-relevant insights. Supporting details for the results presented are available through the cited references. An annotated table of contents allows readers to easily find specific subject matter within the text.

IMPLICATIONS

Over 400 peer-reviewed journal articles and likely more than 1000 presentations resulted from the research conducted through EPA's PM Supersites Program. From the start, the program was developed with a policy focus—providing new information on the accumulation and sources of PM in air on urban and regional scales that might allow for the development of more effective approaches to reducing ambient concentrations of PM to below NAAQS levels. This paper synthesizes and integrates the atmospheric sciences findings from which are interpreted a series of policy-relevant and health-relevant insights developed to support policy decisions on approaches to reduce PM in air and to assist the health-effects and exposure science communities with future research planning.

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INTRODUCTION

In July 1997, the U.S. Environmental Protection Agency (EPA) issued National Ambient Air Quality Standards (NAAQS) for fine particulate matter ($PM_{2.5}$, atmospheric particles with an aerodynamic diameter (AD) less than 2.5 μm).[1] The $PM_{2.5}$ NAAQS were developed by the EPA on the basis of the results of numerous epidemiological studies showing persistent associations between outdoor concentrations of particulate matter (PM) and significant adverse health effects.[2] A detailed understanding of factors influencing human exposure to PM is important for the development of effective emissions control strategies designed to reduce the health impacts of airborne PM.[3] However, considerable uncertainty existed in the late 1990s concerning the mechanisms by which various classes of particles might cause adverse health effects. In part, these uncertainties were due to the need for a more detailed understanding about the composition, concentration, and spatial and temporal distributions of ambient $PM_{2.5}$.

EPA recognized that an improved understanding of key source impacts, development of the most cost-effective emission control strategies, and reduction of health risks associated with $PM_{2.5}$ would depend on an improved characterization of PM in air that was based on having high-quality measurements of $PM_{2.5}$ mass, composition, size, and concentration over a variety of spatial and temporal scales. Yet many $PM_{2.5}$ measurement methods capable of resolving size and composition had not been adequately evaluated or deployed in regulatory or even large-scale research monitoring networks. Recognizing these needs, EPA embarked on an ambitious multilocation air quality research program, commonly referred to as the PM Supersites Program (herein referred to as Supersites Program or just Supersites).[4]

The Supersites Program was established through a series of multiyear, multi-million dollar cooperative agreements and focused on air quality methods, measurements, data analysis, and modeling. The primary goals of the program were:

(1) Conduct methods development and evaluation to compare, evaluate, and help validate emerging and routine methods for characterizing PM. These results would help to define and quantify methods' uncertainty, identify methods suitable for routine monitoring, and to support further the following two objectives.
(2) Characterize ambient airborne PM, its constituent species, and related gaseous pollutants at several locations throughout the United States with differing atmospheric environments to elucidate source-receptor relationships and atmospheric processes leading to PM accumulation on urban and regional scales. These characterizations would provide the scientific foundation for modeling and data analysis efforts that would support the development of State Implementation Plans (SIPs) and more effective risk management approaches.
(3) Support health effects and exposure research on the basis of the data and findings obtained through objectives 1 and 2. This information would help to reduce uncertainty in defining and implementing the NAAQS, and improve the health-exposure research community's ability to address research questions and scientific uncertainties about PM source-receptor-exposure-health effects relationships.

Each Supersites Project, within its study region, integrated a mix of routine and advanced measurements at one or several central locations combined with other monitoring sites. In that sense, a Supersites Project should not be viewed solely as a single site making research-grade measurements, but as part of the overall PM monitoring program. In the case of PM, the Federal Reference Method (FRM) mass network represents the base measurements,

Table 1. Supersites Phase I and II locations and PIs.[a]

Study Location	Institution	PI	E-mail
Atlanta, GA[b]	Georgia Institute of Technology	William Chameides/Armistead (Ted) Russell[e]	No longer at Georgia Tech, ted.russell@ce.gatech.edu
Baltimore, MD[c]	University of Maryland	John Ondov	jondov@wam.umd.edu
Fresno, CA[d]	Desert Research Institute	John Watson and Judy Chow	johnw@dri.edu, judyc@dri.edu
Houston, TX[c]	University of Texas	David Allen	allen@che.utexas.edu
Los Angeles, CA[c]	University of California and University of Southern California	John Froines and Constantinos Sioutas	jfroines@ucla.edu, sioutas@usc.edu
New York, NY[c]	University at Albany, SUNY	Kenneth Demerjian	kld@asrc.cestm.albany.edu
Pittsburgh, PA[c]	Carnegie Mellon University	Spyros Pandis, Allen Robinson, and Cliff Davidson	spyros@andrew.cmu.edu, alr@andrew.cmu.edu, cliff@cmu.edu
St. Louis, MO[c]	Washington University	Jay Turner	jrturner@seas.wustl.edu

Notes: [a]Phase I included funding of the Atlanta and Fresno Supersites Projects in 1999. Phase II included funding of the other Supersites Projects plus continued funding of Fresno beginning in 2000. [b]Phase I. [c]Phase II. [d]Fresno Supersites Project was awarded separate cooperative agreements for both Phase I and Phase II of the project. [e]Armistead (Ted) Russell replaced William Chameides as PI after the completion of Phase II. Dr. Russell is currently PI for Phase III of the project supporting this synthesis of key and policy-relevant insights from the Supersites Program and related studies.

the $PM_{2.5}$ National Chemical Speciation Network the next level of detail, and the Supersites Program the highest level of measurement detail. During the Supersites Program, the $PM_{2.5}$ National Chemical Speciation Network included more than 300 sites, of which 54 were long-term Speciation Trends Network (STN) sites (herein the use of STN will refer to the entire $PM_{2.5}$ National Chemical Speciation Network). Thus, each Supersites Project was supported spatially and temporally by the national criteria pollutant monitoring networks (e.g., ozone [O_3] and $PM_{2.5}$ mass), other national networks (e.g., speciation, acid deposition), and several special studies funded by public and private organizations located within Supersites Project study domains. In return, measurements from the Supersites Program supported the other programs and studies by providing advanced measurements, many at high-time resolution and with detailed chemistry. Descriptions of the individual Supersites Projects, including final reports, are available at the EPA Supersites Program web page (http://www.epa.gov/ttn/amtic/supersites.html).

The Supersites Program consisted of three phases. Phase I efforts were established in 1999 and focused primarily on measurement methods evaluation studies in Atlanta[5] and Fresno.[6] These sites were noncompetitively selected given timing constraints related to parallel deployment of routine elements of the $PM_{2.5}$ monitoring network and by virtue of (1) ongoing and planned research activities that closely aligned with those of the PM Supersites Program, and (2) distinctly different airsheds (e.g., atmospheric chemistry, sources, meteorology, etc.).

EPA initiated the Phase II projects in 2000 after a competitive selection process. The Phase II projects were located in seven urban-focused regional areas in the United States, each with differing atmospheric pollution conditions resulting from variations in source emissions and meteorology. Locations of Supersites projects, principal investigators (PIs), and contact information are listed in Table 1. By design, these projects were hypothesis driven (see final reports for listings), and thus, each had a slightly different emphasis, as shown in Table 2, in addressing the three major program objectives.

During Phase II, coordination of measurements among the Supersites Projects and other studies in the eastern half of the United States led to a coordinated intensive monitoring period in July 2001. This "intensive" effort was fully integrated with stakeholders in local,

Table 2. Supersites Program specific objectives by project.

Supersites Project[a]	Methods Development and Evaluation	Characterize PM and Precursor Species	Support Emissions Control Strategy Development	Support Health-Effects Studies	Evaluate Effectiveness of New Control Technologies
Atlanta	X	X	X[b]		
Fresno	X	X	X	X	
New York	X	X	X		X
Baltimore	X	X	X	X	
Pittsburgh	X	X	X	X	X
St. Louis	X	X	X	X	
Houston		X	X		
Los Angeles	X	X		X	

Notes: [a]With regards to field projects, Atlanta was Phase I only, Fresno was Phases I and II, and the others were only Phase II projects. All Supersites Projects were involved in Phase III activities, including data analysis, development of databases, communication of results through publications, and supporting this synthesis. [b]Supporting emissions control strategy development through modeling began several years after the project and continues today as a Phase III activity, although funding was not provided through the Supersites Program.

Table 3. Integration and synthesis of key findings and policy- and health-relevant insights from the Supersites Program and related studies: science/policy-relevant questions for Supersites Program[a] (project addressing question, related publication).

Synthesis Leads: Paul A. Solomon (EPA), Philip K. Hopke (Clarkson University)

I. Methods

1. What advances have occurred in sampling and analytical methods for measurement of mass, components of mass, semi-volatile species, and precursor species, including integrated, semicontinuous, continuous, and single-particle methods? (Fresno, Chow et al.[21])
   a. What are the analytical characteristics of the methods: uncertainty (precision, accuracy), limits of detection, data capture, reliability?
   b. What have we learned about interferences and the variables that affect those interferences, how are they accounted for in reported data, and how do they affect the uncertainty in the method?
2. Are there routine monitoring techniques that should be instituted so that we will have better information in a few years: (Los Angeles, Solomon and Sioutas[20])
   a. Especially with regards to OC speciation on a routine basis in the networks; and
   b. Continuous methods for mass, and major and minor components (inorganic and organic components)?
3. What biases (uncertainties) exist among methods for mass and chemical components? (New York, see footnote b)
   a. How do we compare data from across different regions or networks using different methods?
   b. Can we identify the biases and develop algorithms to adjust so methods are equivalent?
   c. How do these biases potentially influence PM emissions control strategies?

II. Characterization

4. What is the spatial variation in PM composition and size? (St. Louis, Turner and Allen[417])
   a. How does PM (size and composition) vary at different scales from local to neighborhood, urban, within a region, and among regions?
   b. What are the spatial characteristics of primary vs. secondary PM?
   c. How does PM vary across different regions of the United States and southeastern Canada?
5. What is the temporal variation in PM composition and size? (New York, Demerjian and Mohnen[166])
   a. How does PM (size and composition) vary on differing time scales from subhourly to hourly, daily, by month and season, and over the last half decade?
   b. Are spatial and temporal variations tied together?
   c. How important are peak concentrations in determining relevant averages and which standard is the controlling standard—annual or 24-hr average?
6. What is the spatial and temporal variation in PM precursor species (inorganic and organic)? (Los Angeles, Fine et al.[186])
   a. What is the role of secondary PM and how does it vary spatially and temporally?
   b. What fraction of primary and secondary OC is anthropogenic and natural?
   c. What fraction of the anthropogenic and natural precursor species end up as PM products or as secondary aerosols?
7. What are regional levels of pollutants, how are they transported, and what is their influence on urban and downwind regional levels of PM? (Houston, Allen and Turner[418])
   a. What are the sources of the high levels of organics in cities?
   b. Are they truly higher than the IMPROVE measured organics in rural areas or are the differences just due to monitoring technique differences?
   c. If they are higher, how much of the increase is due to human activity and how much to natural sources?
   d. Conversely, how do urban plumes influence regional levels that may again influence downwind urban and regional areas (e.g., mid-Atlantic influence to the northeast)?
8. What is the influence of transport of anthropogenic and natural PM and PM precursors from outside the United States (e.g., Asian and African dust, major forest fires in Canada, Mexico, and South America) on PM levels within the United States? Can we distinguish natural or exceptional events (e.g., locally generated wind-blown dust from construction, large wildfires from other biogenic combustion sources, Asian or Saharan dust storms from other sources of crustal-related material) from typical air pollution events? (St. Louis, see footnote b)
   a. Do they affect attainment of the 24-hr standards? Annual standards?
   b. What tools are available to distinguish natural or exceptional events?

III. Source Apportionment

9. How well can we identify sources using a range of source apportionment techniques—receptor type models? (Fresno, Watson et al.[303])
   a. Can we assign uncertainties to these results in a realistic way?
   b. Have the techniques been evaluated and can they be validated? If so, how?
   c. How do spatial and temporal variations in emissions (e.g., source profiles) from major source categories influence source apportionment results?
   d. What advantage do high-time resolution methods provide to improving source results from source apportionment methods?
10. What techniques (receptor-type models) can we use to determine the nature and sources of organic aerosols in our nonattainment areas? (Baltimore, see footnote b)
   a. How important are organics in comparison to other constituents?
   b. Can we describe the composition of the organic fraction of the aerosol?
   c. What fraction of EC/BC is anthropogenic and natural?
   d. What are the key organic tracers for source apportionment?
   e. How advantageous are organic tracers for identifying sources over standard chemical composition (e.g., as obtained from STN or IMPROVE)?
   f. How does the use of organic tracers reduce the uncertainty in identifying sources?
   g. What fraction of the organic aerosol is natural vs. anthropogenic and for each of those categories how much is secondary aerosol?
11. What deterministic (emissions-based) air quality models exist and have been evaluated and tested? (Atlanta, Russell[336])
   a. How can air quality model uncertainty be estimated?
   b. What are the uncertainties in these models and their performance on different spatial and temporal scales?
   c. On the basis of model performance, are we including the optimum species (e.g., organic and inorganic aerosol species, gas-phase precursors, and species involved in the oxidant cycle) in the models to adequately account for PM concentrations observed in air?
   d. What and how should we report air quality data so they are consistent with what the models produce in terms of components and spatial and temporal scales?
   e. What have we learned that can give us more or less confidence that the model response is correct?

Table 3. (cont.)

Synthesis Leads: Paul A. Solomon (EPA), Philip K. Hopke (Clarkson University)

IV. Atmospheric Processes

12. What have we learned from high-time resolution measurements and from particle mass spectrometers and other single-particle methods in terms of: (Baltimore, Wexler and Johnston[83])
    a. Atmospheric chemistry,
    b. Relating sources to PM pollution at a receptor, and
    c. Potential for PM exposure?
13. What are the limiting reagents to reduce PM and what are their sources—application of observationally based models? (Pittsburgh, see footnote b)
    a. How do the observed limiting reagents vary spatially by regions and temporally by month or season?
    b. What effect does control of the limiting reagent have on PM concentrations?
    c. For example, does control of NH_3 have the greatest influence on reducing NH_4NO_3 levels?
14. What is the relationship of PM to other pollutants? (Atlanta, Russell[336])
    a. How will NO_x and SO_x reductions influence PM and PM component levels?
    b. What is the influence of current NO_x and SO_x reduction strategies on ozone and PM and PM component levels?
    c. For example, if NH_4NO_3 formation is NO_x-limited, is HNO_3 formation NO_x or VOC-limited and how might controls on NO_x or VOC affect ozone levels locally and downwind, and thus, possibly affect attainment of ozone in effected areas?
    d. What if the regime changes from one limiting reagent to the other, how might this affect emissions reduction strategy development?
15. What role do acid aerosols play in increasing the formation of secondary organics? (Pittsburgh, see footnote b)
    a. If we reduce SO_2 and NO_x emissions, will organic aerosol concentrations decrease?
    b. What about NH_3? Does it also influence organic aerosol concentrations?

V. Emissions Estimates

16. What are the uncertainties in emissions estimates for PM precursors and primary PM components and how do the emissions estimates vary spatially and temporally? (Houston, Simon et al.[338])
    a. What is the fraction of emissions of PM precursors and primary PM components that are anthropogenic (we may be able to control) vs. natural and transboundary (they may be more difficult to control) and how do they vary spatially and temporally?
    b. What improvements have occurred in emissions estimates during the last half-decade?
    c. Have advanced source-apportionment tools allowed for improved top-down verification of emissions estimates?
    d. Are any significant emissions sources inadequately represented in the inventory?

VI. Policy-Relevant Insights (Synthesis)

VII. Health-Relevant Insights (Synthesis)

VIII. What are the Knowledge Gaps and Recommendations for Future Research (Each Paper and Synthesis)

Notes: [a]In retrospect the mention of chemical components or species also includes the physical properties of PM; [b]Insufficient information existed in the literature on the basis of results from the Supersites Program and related studies to develop a technical synthesis paper, although most questions are addressed in part within this integrated synthesis.

state, and federal agencies, including one in Canada, multistate and Regional Planning Organizations (RPOs), and private sector organizations; approximately 30 projects were involved. The success of the initial intensive monitoring program during July 2001 resulted in an agreement among the groups involved to coordinate two additional intensive studies during January and July 2002, although fewer groups were involved in these latter two intensives because fewer studies were planned in 2002. This 13-month effort, inclusive of the three intensive measurement periods, became known as the Eastern Supersites Program (ESP, http://www.epa.gov/ttn/amtic/eastsup.html). An important outcome of the ESP was development of the Supersites Integrated Relational Database (SIRD, http://sird.ce.gatech.edu/), which contains virtually all of the air quality and meteorological data collected within the continental United States from June 2001 to August 2002.[7]

Phase III included five elements: the development of SIRD described above; the NARSTO long-term data archive (http://eosweb.larc.nasa.gov/PRODOCS/narsto/table_narsto.html) that consists of flat files and is not relational; integrated data analysis; publication of results and findings; and the development of this integrated synthesis of key findings and policy- and health-relevant insights. This synthesis is based on the series of 16 science/policy-relevant questions (Table 3) developed cooperatively by EPA, other federal agencies, states, RPOs, and industrial groups. Supersites Program PIs addressed these questions in a series of technical papers published as a special issue of the *Journal of the Air & Waste Management Association* (February 2008). PIs addressed these questions to varying degrees, in part, because of limited information available on some of the topics (n.b., Table 3, Qs 3, 8, 10, 13, and 15).

Over 400 peer-reviewed publications resulted from the Supersites Program. Nearly 180 of these have been published in a series of dedicated special journal issues. Some early results also were published in the special issues associated with the American Association for Aerosol Research (AAAR) PM Meeting held in Pittsburgh, PA, in April 2003 entitled "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health."[8–11] Results covering the entire range of progress during the 5-yr program are included in four dedicated Supersites Program special issues, the initial focusing on the Atlanta Supersites Project[12] and the other three on Phase II projects.[13–15] Four additional special issues[16–19] containing numerous Supersites Program publications resulted from the AAAR PM Supersites Meeting held in Atlanta, GA, February 2005 entitled the "2005 AAAR PM

Supersites Program and Related Studies International Specialty Conference." This conference was designed to support this integrated synthesis, and as such, this paper is intended as a summary of that conference as well. Additional information regarding the two AAAR conferences as well as abstracts and the full conference programs can be found at the AAAR Web site (http://www.aaar.org/index2.cfm?section=Meetings_and_Events&content=Archived_Meetings).

The first part of this synthesis summarizes the published science aligned with three of the major themes associated with the Supersites Program objectives and the program's overall goal: (1) Methods Development and Evaluation, (2) Characterization of Ambient PM, and (3) Estimating Source Contributions at Receptor Locations. The latter section has two major subsections: (a) Receptor-Oriented Approaches, and (b) Source-Oriented Approaches. Results presented in these subsections indicate how receptor-oriented and source-oriented models are being evaluated and applied. The third subsection of the source-oriented models subsection begins to provide insights into how controls of emissions of major precursor species (oxides of nitrogen [NO_x], sulfur dioxide [SO_2], ammonia [NH_3]) might impact PM mass, components, and other related pollutants, such as O_3.

Even though emissions-related science was not a direct objective of the Supersites Program, it was realized that emissions estimation and inventories are critical to modeling PM; therefore, the second part of this synthesis examines the progress made in those areas by the Supersites Program and related studies. The final section of the second part (*Supporting State Implementation Planning*) summarizes progress to date associated with the development of SIPs. Although states and RPOs are involved in these efforts, their initial results already show the importance of findings and data available from the Supersites Program.

Drawing from the science, the conclusions section provides selected policy-relevant and health-relevant insights and a listing of some major knowledge gaps that still need to be addressed. The goal of the first two sections in the conclusions section is the interpretation of the atmospheric sciences findings in terms of: (1) policy-relevant insights of use to air quality managers and decision makers, and (2) health-relevant insights based on interpretation of the atmospheric sciences findings to provide future directions for health and exposure scientists. Air quality managers can use these findings and insights to develop more effective emissions management strategies to address current and future PM NAAQS as well as sampling network planning and implementation while assisting the health and exposure scientists to better plan studies to understand the adverse effect of PM on human health. The final section of this part of the synthesis addresses knowledge gaps, and offers suggestions of what still needs to be learned to reduce further uncertainties in our understanding of atmospheric processes, the accumulation of PM in air on urban and regional scales, and associated source-receptor relationships. Finally, given the scope and depth of research and findings from the Supersites Program, this paper is intended as a reference source for decision- and policy-makers and scientists to provide a general understanding of the overall research conducted and its policy- and health-relevant insights. A comprehensive bibliography also is provided so additional information can easily be found as needed.

METHODS DEVELOPMENT AND EVALUATION

As a direct result of the Supersites Program, significant advances have been made in the development and evaluation of new and existing methods to quantify PM mass, composition, physical properties, and precursor species. The primary focus of the methods development and evaluation was on continuous and semicontinuous methods (subsequently referred to as continuous). Two comprehensive reviews of methods research from the Supersites Program and related studies have been prepared and support this synthesis.[20,21] Solomon and Sioutas[20] evaluated results from the evaluations performed through the Supersites Program and related studies in terms of which methods might be ready for routine monitoring networks or that might require additional evaluation within research monitoring networks. Chow et al.[21] focused on analytical characteristics quantified from the methods evaluation studies. These reviews complement and update earlier reviews on PM measurement methods by Chow,[22] Solomon et al.,[23] McMurry,[24] and Fehsenfeld et al.[25]

Several new methods were developed as a direct result of the Supersites Program, as listed in Table 4. These included new filter-based and continuous methods for determining mass, chemical composition, and physical properties of ambient PM.

Time-Integrated Filter-Based Methods

Standard reference materials (SRMs) are not available for determining the accuracy associated with the measurement (including sample collection and analysis) of most components or physical properties of PM. Therefore, in most cases only bias or comparability are determined by the congruence of several methods measuring the same or similar parameters, also typically of unknown accuracy.[25] Accuracy is the difference between a reference standard (e.g., SRM) and the test method, whereas bias is a systematic difference between a historically accepted method and the test method. Time-integrated filter-based methods (referred to within as integrated methods) have been thoroughly evaluated over the last 30 plus yr, and reasonable to significant confidence exists in these methods.[22,25] Thus, they were often used during the Supersites Program as the benchmark by which to judge the suitability of and develop uncertainty estimates for the emerging advanced methods. However, care is needed to obtain data of high quality with integrated methods.

PM Mass and Components. A variety of integrated methods to measure mass and PM composition were evaluated during the Atlanta Supersites Project.[26] Methods included the FRM for mass and EPA's prototype chemical speciation samplers as well as research samplers designed to minimize sampling artifacts (e.g., volatilization losses) associated with the collection of PM mass and components using filter-based methods. Resulting uncertainty estimates are provided in Table 5.

Table 4. New methods or first full-scale field tests of new methods resulting from Supersites Program and related studies.[a]

Parameter/Method	Supersites Project	Reference
Filter-based integrated methods		
High-volume (550 L/min) UF PM and accumulation-mode mass monitor, time-integrated	Los Angeles	Misra et al.[449]
High-volume organic compound speciation sampler with 3-hr time resolution	Baltimore	Ondov et al.,[450] Rogge[64]
Portable dilution chamber sampler (emissions testing)	Pittsburgh	Lipsky and Robinson[451]
Continuous and semicontinuous methods		
Continuous PM_c mass	Los Angeles	Sioutas and Solomon,[98] Misra et al.[97,452]
Continuous UF PM mass	Los Angeles	Chakrabarti et al.[99]
Size-fractioned continuous $PM_{2.5}$ particle nitrate monitor (Cascade Integrated Collection and Vaporization System [ICVS])	Los Angeles	Fine et al.[453]
Particle-into-liquid sample—ion chromatography (PILS-IC)	Atlanta	Weber et al.[123]
SEAS	Baltimore	Kidwell and Ondov[153,154]
PBW (DAASS)	Pittsburgh	Stanier et al.[117]
Particle density	Atlanta	McMurry et al.[24]
WCPC	Aerosol Dynamics, Inc./Los Angeles	Biswas et al.,[109] Hering et al.[107]
Algorithm to combine aerosol size distributions collected with different instruments (nano-SMPS, SMPS, and APS), 3 nm to 10 μm	Pittsburgh	Khlystov et al.[102]
Particle mass spectrometer with VACES to improve particle counting efficiency	Pittsburgh/Los Angeles	Khlystov et al. (AMS),[454] Zhao et al. (RSMS)[223]
Particle mass spectrometers	Atlanta	Middlebrook et al.[159]

Notes: [a]Table 6 provides a detailed listing of continuous measurement methods research conducted as part of the Supersites Program.

Results from the Supersites Program and related studies, operating in multiple locations under a wide range of conditions, continue to reaffirm that the FRM is prone to loss of semi-volatile components (i.e., ammonium nitrate [NH_4NO_3], semi-volatile organic carbon [SVOC]) (e.g., Hering and Cass,[27] Pang et al.,[28] Solomon et al.,[26] Long et al.,[29] Jaques et al.,[30] Lee et al.,[31] Chow et al.,[32] Grover et al.,[33] Schwab et al.,[34] Wilson et al.,[35] Zhu et al.,[533] and references within these publications). Because cool, humid conditions tend to stabilize semi-volatile material (SVM),[35] larger losses are observed in the summer (almost no loss in the winter) and during the day.[32,36–38] Urban sites may have greater loss than rural sites, possibly because of a more volatile, less processed aerosol near emissions sources.[34] However, the $PM_{2.5}$ FRM is a regulatory standard designed to judge compliance with the health-based PM NAAQS and not an analytical standard designed to determine the "true" mass concentrations relative to what is actually in the air.[25] The fact that health and air quality associations have been based on available measurement technologies, often similar to the FRM, provides a rationale supporting the use of the current FRM.[1,2] However, because FRM mass collected with Teflon filters does not always include SVM and because people are likely to breathe total mass without the same sampling artifacts, health-related datasets are probably not a test of whether the SVM is health relevant or not. Thus, future health-relevant monitoring programs should begin to use monitors that measure total mass or nonvolatile and SVM mass separately.[35]

At the New York Supersite (Queens), samples were collected during the summers of 2001 and winter of 2004 using a 42-L/min sampler (Hi-flo) that allowed for the collection of 6-hr $PM_{2.5}$ samples throughout the day.[39,40]

Table 5. Uncertainty estimates reported for integrated and continuous methods evaluated during the 1999 Atlanta Supersites Project.

Species	Uncertainty Range	Comment	Reference
Time-integrated filter-based samplers			
Mass	±20%		Solomon et al., 2003[26]
Sulfate	±10%		
Nitrate	±30–35%		
Ammonium	±10–15%		
OC (1)	±20%	(1) With or without denuders	
OC (2)	±35–35%	(2) With and without denuders	
EC	±20–200%	Lower range same analytical method, upper range using different TOA analytical methods	
Minor and trace elements	±20–30%		
Continuous methods			
Nitrate	20–30% (~0.1–0.2 μg/m^3)	Study average concentration about 0.5 μg/m^3	Weber et al.[124]
Sulfate	10–15%		Weber et al.[124]
TC, OC, EC,	7, 13, 26%		Lim et al.[147]
Particle mass spectrometers	Generally consistent particle classifications	Difficult to compare in classical sense, see Middlebrook et al.,[159] for details.	Middlebrook et al.[159]

The samples were analyzed for water- and acid-soluble elements by inductively coupled plasma-mass spectrometry (ICP-MS).[41] Sulfate also was determined from the aqueous extract by ion chromatograph. The sampler was compared with a commercial samplers with excellent agreement (regression slopes within 3% of unity) for sulfate and several trace elements.[40]

At the Pittsburgh Supersite, Pekney and Davidson[42] developed a modified microwave-assisted digestion procedure to analyze trace elements by ICP-MS and achieved good agreement with the certified values in National Institute for Standards and Technology (NIST) SRM 1648 urban dust.

Measurement of carbonaceous PM components remains a significant challenge, complicated by the many organic species (hundreds to thousands) found in air and their wide range of physical and chemical properties. The two main issues associated with the measurement of the empirically defined major components of carbon (organic carbon [OC] and elemental carbon [EC]) found in atmospheric aerosols and typically collected by quartz-fiber filters are: (1) quantifying sampling artifacts (or appropriate blank values), and (2) the analysis of the sample on the filter by different thermal or thermal optical analysis (TOA) methods, such as those used during the Supersites Program (e.g., National Institute for Occupational Safety and Health [NIOSH]—Birch and Cary,[43] EPA's STN—Peterson and Richards,[44] Interagency Monitoring of Protected Visual Environments [IMPROVE]—Chow et al.,[44,45] ACE-Asia—Mader et al.[47]). Again, standard methods have not been established nor are SRMs available to provide a basis for standardization. Carbonate carbon (CC) also can be measured by the TOA method, although for $PM_{2.5}$ CC concentrations usually are not significant. Differences as high as a factor of 2 are observed for EC when comparing results between NIOSH (or STN) and IMPROVE. However, results within 20% often are obtained when comparing similar methods.[26,46,48] Consistent measurements of EC are important because EC in many urban areas is primarily emitted by diesel engines and thus is used often as a tracer for motor vehicle diesel emissions in receptor modeling studies. Supersites Program results also reaffirm that negative sampling artifacts (loss of SVOC during or after collection) are small (<10% of the collected OC), but positive artifacts (absorption or adsorption of gas-phase organic species by the collection filter) can be significant, approaching 50% or more of the collected OC,[26,49,50] with absolute values of the artifact ranging from less than 1 to 4 $\mu g/m^3$.

A third uncertainty associated with quantifying carbonaceous material in PM is the conversion of OC to organic matter (OM), the latter including other elements that compose the organic molecules (e.g., hydrogen, oxygen, nitrogen, sulfur). Results from the suburban St. Louis Supersite[51] indicated a 2-yr annual average OM/OC ratio of approximately 1.8–1.9, depending on the approach (reconstructed mass balance using major components except OC vs. source apportionment) with summer being slightly higher and winter slightly lower. In Pittsburgh, similar values were obtained, which varied by organic polarity based on extraction by different solvents and also varied by season.[530] Turpin and Lim[52] provide a thorough review of this uncertainty. In New York, the reconstructed mass balance approach was used at a rural and an urban site.[53] The 3-yr average OM/OC ratio was between approximately 1.5 and 1.9 at the rural site and approximately 1.3 and 1.6 at the urban site. The ratio was higher in the summer at the rural site (~2.1–2.3) than in the winter (1.6–1.7). Little seasonal variability was observed at the urban site, often influenced by fresh emissions of organic compounds from vehicle exhaust.

The use of OC denuders appears to minimize the positive sampling artifact, although they may enhance the negative artifact. At least two denuders appear suitable for network operations, the carbon-impregnated filter (CIF) denuder[54] and the monolith or honeycomb carbon denuder,[50] although additional evaluation is needed to fully understand their characteristics under a wide range of environmental and pollution conditions. Other simpler approaches have been recommended that include the use of a quartz-fiber backup filter behind either a Teflon filter (e.g., the one used for mass)[50,52] or behind the current quartz-fiber filter.[49,50] Alternate approaches using statistical methods to estimate the blank also are being pursued.[55–58]

OC Species. Samples for determining ambient concentrations of individual organic species in PM typically were collected for 24-hr sampling periods using medium- to high-volume sampling systems. As recently as 5–7 yr ago, composite samples collected over several sampling periods (e.g., seasonally) were needed for OC speciation analysis.[59–61] High volume sampling and improvements in analytical methods have allowed analysis of OC species on 24-hr samples without compositing a series of filters.[62,63] As part of the Baltimore Supersites Project, sampling periods as short as 3 hr were achieved,[64] as described below, allowing examination of the diurnal variation in many individual organic compounds.

Samples are most often collected on quartz-fiber or Teflon filters with or without preceding denuders or polyurethane foam (PUF) plugs behind the filter (e.g., denuder-filter-PUF). Filters (and PUF plugs) are extracted with a variety of organic solvents and/or derivatives are formed following extraction (e.g., methylation of acids with diazomethane and trimethysilyation of alcohols) to allow nonpolar or a limited number of polar compounds, respectively, to be determined by gas chromatography (GC)-mass spectrometry (MS) or other recently used methods.[65] More than 100 organic species are determined routinely by these time-intensive analysis approaches.[59–62,66]

Recently, advanced methods to quantify oxygenated compounds containing one or more hydroxyl, one or more carboxylic acid functional groups, or both have been developed.[63,65,66–68] Although others used a variety of different extraction methods followed by GC-MS, Gao et al.[65] used a simple extraction method (methanol) with identification and quantification using four analytical techniques: liquid chromatography MS, ion trap MS, laser desorption ionization MS, and high-resolution MS. Forty distinct species were detected with clues provided as to the structure of the species by each analysis method. Furthermore, some of the polar organic compounds have

been identified through laboratory studies and their presence confirmed in ambient particles as possible tracers for biogenic and anthropogenic secondary aerosols; for example, monoterpenes and toluene.[65,69,70]

Subsets of organic compounds for specific purposes also were measured. Cho et al.[71] developed an extraction-derivatization method (dichloromethane [DCM]-acetic anhydride) with analysis by GC-MS to determine the concentrations of four quinones in $PM_{2.5}$, toxicologically important because of their ability to generate reactive oxygen species (ROS) and to form covalent bonds with tissue macromolecules. The four quinones determined were 1,2-naphthoquinone (1,2-NQ), 1,4-naphthoquinone (1,4-NQ), 9,10-phenanthraquinone (9,10-PQ), and 9,10-anthraquinone (9,10-AQ). They quantified the concentrations of these four quinones in diesel exhaust particles (DEPs), in NIST SRM 1649a at μg/g levels, and in ambient $PM_{2.5}$ samples at pg/m^3 concentrations. Precision (repeatability and reproducibility) of these measurements varied from 2 to 22%. The samples were collected at one rural and two urban sampling locations upwind, within, and downwind of major emission sources in Los Angeles, CA. Among these four quinones, 1,2-NQ had not been previously reported in ambient PM.

Xia and Hopke[72] determined the seasonal variation in the concentrations of 2-methyltetrols (2-methylthreitol and 2-methylerythritol) in ambient air in Potsdam, NY, using a standard extraction-derivatization method followed by GC-MS. The size distribution of organic functional groups (carbonyl, aliphatic, and organonitrate) were determined in eight size ranges (<50 nm to 4 μm) in ambient PM samples in Houston, TX, collected using the Hering low-pressure impactor.[73,74] Functional groups were then determined directly on the impactor substrates (zinc [Zn]-selenide) using transmission-mode Fourier transform infrared spectroscopy (FTIR). Of interest was that all three functional groups exhibited a maximum in the 2- to 4-μm size range, not seen previously in Los Angeles.[75,76]

Miguel et al.[77] measured various polyaromatic hydrocarbons (PAHs) in ultrafine, accumulation-mode, and coarse-mode ambient PM samples in Claremont, CA. Samples were extracted in DCM and analyzed by high-performance liquid chromatography-fluorescence. From October to February, most of the mass of PAHs determined was in the ultrafine and accumulations modes; however, from March to July a significant fraction of the PAHs were found in the coarse mode. This was unexpected because the PAHs are derived from combustion and expected in the ultrafine or accumulation mode. Additional details of the analysis methods can be found in the literature (e.g., Rogge et al.,[78] Schauer and Cass,[62] Saxena and Hildemann,[79] Cass,[80] Puxbaum,[81] and in the literature cited above). Fine et al.[82] also measured organic species in the ultrafine and accumulation modes. They observed hopanes, an indicator of motor vehicle exhaust, to be mostly in the ultrafine mode; cholesterol, an indicator of meat cooking and possibly sea spray, in the ultrafine mode and in larger particles, respectively; levoglucosan, an indicator of wood burning, to be in both the ultrafine and accumulation modes, but mostly in the latter; and 1,2-benzenedicarboxylic acid, an indicator of secondary organic aerosol (SOA), mostly in the accumulation mode. The latter varied by site, season, and time of day as expected if formed by photochemical processes.

Organic species were measured in 24-hr $PM_{2.5}$ samples at Supersites Projects in Houston, TX; Los Angeles, CA; Pittsburgh, PA; St. Louis, MO; Fresno, CA; and Atlanta, GA. The main purpose of these measurements was for use in source apportionment studies, as briefly summarized later in this paper. Of special interest are the measurements at the Baltimore Supersites Project (Ponca St.). Here 3-hr $PM_{2.5}$ samples were collected using a specially designed sampling system that consisted of five parallel sampling channels, each operating at 600 L/min.[64] Eight samples were collected in series during a 24-hr period for 57 days scattered throughout the 9.5-month field project. Samples were collected on quartz-fiber filters followed by a PUF plug. After collection, filters and PUF plugs were maintained below 21 °C until chemical analysis at Florida International University (FIU).[534] Previously used procedures were used for extraction and analysis of the collected samples (e.g., Rogge et al.[78]).

Continuous Methods

Development and evaluation of continuous methods was a major objective at most Supersites Projects and all have applied continuous methods to characterize PM. Continuous methods developed or first evaluated within the Supersites Program are listed in Table 4. Comprehensive reviews of methods research from the Supersites Program and related studies are given in Solomon and Sioutas[20] and Chow et al.[21] A listing of continuous measurement methods developed and/or evaluated during the Supersites Program and related studies, is provided in Table 6, which summarizes material presented in Solomon and Sioutas.[20] Wexler and Johnston[83] provide a summary of lessons learned from the application of continuous methods as applied during the Supersites Program. A summary of findings based on the evaluations conducted through the Supersites Program and related studies is discussed below for mass, physical properties, and chemical composition, the latter further divided into categories for ions, carbon, and trace elements.

Mass. The tapered element oscillating microbalance (TEOM) is the most widely used continuous mass monitor within the United States. The original version was heated to 50 °C to stabilize measurements against changes in ambient temperature and to limit interferences from particle-bound water (PBW).[84] However, loss of SVM because of heating the sample has been widely noted, resulting in the development of modified versions. As the Supersites Program began, three commercial methods became available (the sample equilibration system [SES[85]], differential TEOM [D-TEOM[86]], and the filter dynamics measurement system [FDMS[87]]) and each was thoroughly evaluated during the Supersites Program. The SES-TEOM was well correlated with the FRM,[88–90] indicating both had similar losses of SVMs. The SES-TEOM was higher than the standard TEOM (50 °C) but lower than the real-time ambient mass sampler (RAMS), which measured semi-volatile species, excluding water, whereas the other samplers lost part or all of the semi-volatile component of the collected

Table 6. Summary of continuous measurement methods developed and/or evaluated during EPA's PM Supersites Program and related studies.[20a]

Measurement Method	Basis of Measurement	Methods Used for Comparability Tests (considered reference sampler*)	Qualitative Summary of Comparability Findings (details are provided in cited references)	Comments/References (vendor used in study)
		PHYSICAL PROPERTIES OF PM		
GRAVIMETRIC METHODS FOR PM MASS				
TEOM-Based Methods[84]				
RAMS	Uses a particle concentrator, several denuders and diffusion dryers to remove interfering species and water, and a TEOM detector with a "sandwich-filter" to retain SVM.	Field tests (Multiple locations and different sampler combinations) PC-BOSS* TEOM (30 °C, 50 °C) FRM $PM_{2.5}$ Partisol CAMM RAMS URG MASS	Salt Lake City—comparable with PC-BOSS with excellent agreement $r^2 > 0.9$, slope ~1, zero intercept for both 24-hr and 1-hr average data. TEOM lower by 31% (winter) and 42% (summer), FRM low during low, dry, warm periods. Houston and Seattle—good agreement among continuous methods. CAMM and RAMS typically higher than integrated samplers and heated TEOM.	Method[455–457] Laboratory[29,89] 50 °C TEOM likely good estimate of non-volatile $PM_{2.5}$ mass.
SES TEOM	TEOM operated at 30 °C with a Nafion dryer to remove residual moisture.	(a) Laboratory tests (b) Field tests (Multiple locations) RAMS* CAMM FRM TEOM	(a) Sensitive to changes in RH, although less than TEOM at 50 °C. (b) RAMS reported higher values than the SES TEOM and FRM. SES TEOM agreed with FRM, suggesting loss of SVM from both; seasonal differences noted.	Method[85] Laboratory[94] Field[88,89,93] (R&P, now Thermo Fisher Scientific, Inc., Franklin, MA)
D–TEOM	TEOM operated with a diffusion dryer and electrostatic precipitator in series to remove water and particles from air stream; cycling with electrostatic precipitator on and off in 5-min intervals allows on-period to act as a blank for off-period.	(a) Laboratory tests (b) Field tests (Claremont, CA) MOUDI* Dichotomous Partisol (Rubidoux, CA) RAMS* CAMM FRM Partisol Harvard Denuder*—for artifact-free NH_4NO_3 Also see FDMS	(a) Loss of mass from TEOM filter on longer time scale than 5-min cycle time of electrostatic precipitator (on/off), confirming self-referencing capabilities. No interferences from SO_2 and NO_2. NH_4NO_3 measured with minimal loss. (b) Claremont—high precision (collocated D-TEOM) obtained on 24-hr averaged data ($r^2 > 0.94$); $PM_{2.5}$ D-TEOM (18%) > MOUDI (17%) > Partisol, but well correlated ($r^2 > 0.8$). Rubidoux—$PM_{2.5}$ D-TEOM > RAMS > CAMM > FRM; at low concentrations D-TEOM significantly higher (factor of 2) than RAMS, but at high concentration (>30 $\mu g/m^3$) similar values reported, although data limited at high mass concentrations. Semi-volatile species (e.g., NH_4NO_3 and SOA collected by D-TEOM and not RAMS or CAMM), although RAMS at low concentrations may be low because of poor concentration efficiency of sampler and not loss of volatile species.	Method[86] Laboratory[34,92,94] Field[30,31,34,92] Negative mass measured when electrostatic precipitator is turned on provides estimate of loss of SVM as confirmed by comparison to nitrate by R&P 8400N.[31,92] D-TEOM provides good estimate of $PM_{2.5}$ mass under high nitrate conditions on a near-continuous basis.[30,92,94] No longer commercially available. (R&P)

Table 6. (cont.)

Measurement Method	Basis of Measurement	Methods Used for Comparability Tests (considered reference sampler*)	Qualitative Summary of Comparability Findings (details are provided in cited references)	Comments/References (vendor used in study)
		PHYSICAL PROPERTIES OF PM (cont.)		
GRAVIMETRIC METHODS FOR PM MASS (cont.)				
TEOM-Based Methods (cont.)				
FDMS-TEOM (FDMS)	Similar to D-TEOM, but uses a cold filter (4 °C) to remove particles rather than electrostatic precipitator; cycling between ambient and particle-free air in 6-min intervals allows the particle-free air to act as a blank for ambient measurements.	Field tests (Lindon, UT) TEOM (30 °C) D-TEOM RAMS* PC-BOSS* (Rubidoux, CA) TEOM (50 °C) RAMS* PC-BOSS* R&P 8400N (nitrate) Sunset OC/EC (Queens, NY) BAM FRM Reconstructed mass	FDMS and D-TEOM operated well. FDMS and D-TEOM both agreed well with PC-BOSS and RAMS, but FDMS had slightly better agreement (within 3%) on average and much better during peak events (D-TEOM lower than FDMS by ~21 $\mu g/m^3$ (on average). 30 °C and 50 °C TEOM units reported lower values than FDMS and SES. Difference between FDMS-TEOM and 50 °C TEOM approximately equal to sum of SVOC and NH_4NO_3. Typically higher mass values relative to simple filter-based methods (e.g., FRM) and difference approximately equal to direct measure of SVM suggests improved measurements by both FDMS and D-TEOM. FDMS and BAM agree well (~2% on average) in New York and both are ~25% higher than FRM.	Method[87] Field[33,34] Difference between 50 °C TEOM and FDMS was approximately equal to SVM, suggesting a potential continuous method for measuring the semi-volatile component of $PM_{2.5}$ mass or direct measure of non-volatile $PM_{2.5}$ mass. FRM only lost part of the semi-volatile mass. (R&P)
PM_c TEOM	Uses a virtual impactor with a minor flow fraction of 4% of total flow to separate $PM_{2.5}$ and PM_c with a TEOM as the detector for PM_c particles, operating at a total flow of 50 L/min and 50 °C. Most recent version uses the TEOM to detect both $PM_{2.5}$ and PM_c and includes FDMS technology to minimize loss of semi-volatile components in both $PM_{2.5}$ and PM_c.	Field tests (Los Angeles) MOUDI (Multiple locations) Difference method* (PM_{10} FRM − $PM_{2.5}$ FRM mass) PM_c BAM (16.7 L/min dichotomous with 10% minor flow fraction) APS	PM_c mass highly correlated ($r^2 >$ 0.85 in Los Angeles, > 0.95 in four cities). Ratio of PM_c TEOM to FRM difference low by 10–30% because of loss of semi-volatile species and low inlet cutpoint (9 μm). In more recent studies the cutpoint was increased and the temperature of the TEOM was reduced to 35 °C. APS had good agreement (r^2 and slope close to 1) to FRM difference method for PM_c at western locations. Water seemed to be an issue at the eastern locations.	Method[97] Field[97,100] PM_c TEOM under evaluation for use in EPA as an FEM for the PM_c monitoring network. Additional studies underway with modified samplers, including PM_c FDMS-TEOM method. (R&P)
BAM-Based Methods				
PM_c BAM	Uses a virtual impactor with a minor flow split of 10% to separate $PM_{2.5}$ and PM_c with dual BAM detectors to measure $PM_{2.5}$ and PM_c particles simultaneously; operates at a total flow of 16.7 L/min.	Field test (Four cities) PM_c TEOM FRM difference* (PM_{10} FRM − $PM_{2.5}$ FRM mass) PM_c BAM (16.7 L/min dichotomous with 10% minor flow fraction) APS	PMc BAM had reasonable agreement with a ratio close to 1 and $r^2 >$ 0.8, but $PM_{2.5}$ was significantly overestimated. APS had good agreement (r^2 and slope close to 1) to FRM difference method for PM_c at western locations. Water seemed to be an issue at the eastern locations.	Method[100] Method BAM[458] Field[100] PM_c BAM under evaluation[100] for use in EPA as an FEM for the PM_c monitoring network. Additional studies underway with modified samplers. (Tisch Environmental Inc.)

Table 6. (cont.)

Measurement Method	Basis of Measurement	Methods Used for Comparability Tests (considered reference sampler*)	Qualitative Summary of Comparability Findings (details are provided in cited references)	Comments/References (vendor used in study)
		PHYSICAL PROPERTIES OF PM (cont.)		
GRAVIMETRIC METHODS FOR PM MASS (cont.)				
BAM-Based Methods (cont.)				
UF BAM	BAM with a 0.15-μm cutpoint virtual impactor designed with a low pressure drop.	Field tests SMPS MOUDI	UF BAM and MOUDI had excellent agreement ($r^2 = 0.92$; slope = 0.97) with 2-hr sampling; SMPS underestimated UF BAM because of assumptions used to calculate mass from SMPS data.	Method[99] Field[99] UF mass and $PM_{2.5}$ mass did not correlate, and UF mass and UF number concentrations did not correlate, thus, showing the need for a direct UF mass measurement.
Pressure-Drop-Based Methods				
CAMM	Measures increase pressure drop across a membrane filter as particles load the filter; air is first dried to 40% RH and the tape is advanced every 30–60 min, both of which minimize semi-volatile losses; the pressure drop is proportional to the deposited PM.	Field tests (Multiple locations) HI (24-hr average data) D-TEOM SES TEOM RAMS	Seven cities: comparison with HI—concentration ratio of 1.07, $r^2 = 0.90$. Comparable results in Houston and Seattle for RAMS and 30 °C TEOM; CAMM slightly higher. Continuous samplers higher than integrated likely because of loss of SVM from integrated samplers. Rubidoux: D-TEOM > RAMS > CAMM. Three eastern cites: continuous samplers varied by 10–30%; CAMM lower than SES TEOM and FRM.	Method[459] Field[31,88,89,459] (Thermo Andersen, now Thermo Fisher Scientific Inc., Franklin, MA)
INDIRECT METHODS FOR MASS CONCENTRATION[b]				
SMPS-APS	Uses a DMA and CPC to obtain size distribution of particles in the range from ~10 to 800 nm; APS obtains a size distribution from ~0.5 to 10 μm or higher; combined size distribution is then converted to mass concentration on the basis of assumptions of particle density and shape factors.	Field test MOUDI Partisol ($PM_{2.5}$ and PM_{10}) $PM_{2.5}$ BAM	Agreement within 20% for $PM_{2.5}$; SMPS-APS estimated PM_{10} data low compared to Partisol, likely due to low counting efficiency of APS in upper PM_c range; MOUDI UF mass and SMPS UF mass had poor agreement, possibly due to particle bounce in the MOUDI; SMPS-OPC agreed but was high by 20% to $PM_{2.5}$ BAM.	Field tests[101,102,280] Data suggest APS may not be useful for obtaining PM_c data because low counting efficiencies for particles in the PM_c size range (5–10 μm). (Multiple vendors)
SIZE DISTRIBUTION AND NUMBER CONCENTRATION[c]				
WCPC	Uses water rather than butanol to saturate particles by condensation, which allows for optical counting of particles. Wetted condenser walls are warmer than the air entering the condenser; butanol CPC has cooler walls.	Field tests Butanol CPC*	Prototype model 3785 has good agreement between detection limit and 40,000/cm^3, ratio drops to 0.6–0.8 between 40,000 and 100,000/cm^3. Model 3786 measuring UF PM particles showed good agreement up to 100,000/cm^3.	Method[107,108] Field[109,110] Model 3786 measures UF PM with a lower size cut of 2.5 nm and an extended concentration range up to 100,000/cm^3.[110] Model 3782 is similar to 3785 but has an extended concentration range above 40,000/cm^3. Model 3781 is a low-cost model with a 6-nm lower size cut and concentration range of 100,000/cm^3. (TSI Inc.)

Table 6. (cont.)

Measurement Method	Basis of Measurement	Methods Used for Comparability Tests (considered reference sampler*)	Qualitative Summary of Comparability Findings (details are provided in cited references)	Comments/References (vendor used in study)
		PHYSICAL PROPERTIES OF PM (cont.)		
SIZE DISTRIBUTION AND NUMBER CONCENTRATION (cont.)				
Nano-SMPS	Uses a shorter-length DMA (nano-DMA) along with a CPC to count particles in the size range between ~2 and 150 nm.			Method (TSI, Inc., Model 3085 nano-DMA) See references associated with method to estimate PBW content. (Multiple vendors)
DENSITY AND PBW				
Density (effective)	DMA-APM first selects particle on the basis of electrical mobility (DMA) and then mass by APM. ELPI measures particle mass by first measuring AD followed by an SMPS that measures mobility diameters.	Field tests DMA-APM ELPI-SMPS	DMA-APM and ELPI-SMPS agreed to within 10% for aerosols of known density and within ~5% for ambient aerosols. ELPI-SMPS provided reasonable estimates for known submicron aerosols.	Method[24] Laboratory[113] Field[112,113] Density also often estimated based on particle composition.
PBW	DAASS: nano-SMPS, SMPS, and APS are operated in parallel with overlapping size distributions from 3 nm to 10 μm; system samples ambient and dry (30% RH) size distributions on a 7-min cycle; absolute water content of the aerosol is obtained every 15 min.	Laboratory tests $(NH_4)_2SO_4$ at different RH values Field tests Modeled based on measured chemical composition and PM mass (SES TEOM); Nephelometer light scattering calculations	GFEMN and AIM models underpredicted aerosol water content by ~36–37%. Good agreement of water content on the basis of calculation from light scattering.	Method[117] Laboratory[117] Field[117,119] Historical method: Two DMA units in series, one operated under dry conditions, the other at RH approaching 90%. Measures at specific particle sizes, not a size distribution. Difference between measured particles of a given initial size under dry and ambient conditions provides estimate of growth factors. Particles are classified as more or less hygroscopic.
CHEMICAL COMPOSITION OF PM				
ANION AND CATION MONITORING				
Methods Based on Thermal Reduction with Detection by Gas Analyzers				
ICVS	Particles are grown by humidification and impacted on a metal strip. After 8 min the strip is flashed at high temperature to vaporize collected PM. Generated gases (SO_2, NO_x) are then measured by appropriate gas analyzers. Separate systems are used to measure nitrate and sulfate, each with 10-min time resolution.	(a) Laboratory tests NH_4NO_3 aerosol (b) Field tests Filter packs (Teflon/nylon) Harvard/EPA annular denuder system (HEADS) Magnesium oxide denuder/nylon	(a) Collection efficiencies for generated NH_4NO_3 particles were > 95% for particles > 0.1 μm. Evaporative losses for NH_4NO_3 were 2 ± 4%. (b) Good agreement was observed with the prototype instrument in comparison to denuder filter-based methods in three western locations ($r^2 > 0.97$, slopes 0.96–1.06), detection limit 0.4 μg/m^3. Evaluations in several other locations using the next generation or commercial unit consistently found lower recoveries by 20–40% relative to denuder filter-based methods or other continuous methods such as PILS-IC. In addition, the method becomes nonlinear compared with filter-based and other continuous methods above ~2 μg/m^3.	Method[121,460] Laboratory[121] Field[33,121,125,126,461,462] Several investigators calibrated 24-hr average ICVS data to filter data and then used those calibration values to obtain adjusted hourly data, which suggests a useful method for obtaining continuous data using the ICVS systems (nitrate—Model 8400N, sulfate—Model 8400S). The 8400S and 8400N are no longer available from Thermo Fisher Scientific, Inc., formerly R&P. (R&P)

Table 6. (cont.)

Measurement Method	Basis of Measurement	Methods Used for Comparability Tests (considered reference sampler*)	Qualitative Summary of Comparability Findings (details are provided in cited references)	Comments/References (vendor used in study)
		PHYSICAL PROPERTIES OF PM (cont.)		
CHEMICAL COMPOSITION OF PM (cont.)				
ANION AND CATION MONITORING (cont.)				
Methods Based on Thermal Reduction with Detection by Gas Analyzers (cont.)				
Cascade ICVS	Size-resolved particles humidified and collected on three impactor stages in a cascade impactor to obtain continuous size-resolved (1–2.5, 0.5–1, 0.08–0.5 μm) nitrate data.	Field tests (Multiple sites in Los Angeles) MOUDI HEADS (Harvard)	$PM_{2.5}$ nitrate and size-resolved nitrate were compared. Nitrate was greater by cascade ICVS then MOUDI, suggesting loss of NH_4NO_3 in MOUDI. The cascade ICVS was about 10% more than the HEADS $PM_{2.5}$ nitrate.	Method[453] Field[453]
ARA	Uses a three-channel continuous differencing approach with detection by a NO_x analyzer with Mo converter. Includes a series of two annular and two carbon honeycomb denuders to remove interfering gases. Channel 1 is the system blank, channel 2 includes all particulate nitrogen species plus blank measured in channel 1, providing a measure of total nitrate. Ammonium with nitrate is measured in channel 3. In all three channels NO is measured as the end product.	Field tests PILS-IC PPD Sampler SJAC Denuder filter-based*	Atlanta: all continuous methods agreed to within 20–35% of each other and within 10–25% of filter-based methods; however, ARA was the least correlated ($r^2 < 0.3$) and had the greatest difference from the mean of the methods, although this might be due to the very low nitrate concentration (0.5 $\mu g/m^3$ on average observed during the study)[5] in light of a difference method against a relatively high background of NO_x.	Method[463] Field[124] Refined versions of this research method have been used with good operational success in SEARCH in the southeastern United States since about 1999, although published comparisons to other methods are still needed.
Thermo-Electron/ Harvard	Continuous-flow sulfate monitor involving conversion of sulfate to SO_2 by thermal reduction on stainless steel at ~900 °C with detection by an SO_2 analyzer.	Field tests (Preproduction method) R&P 8400S PILS-IC AMS	Recoveries range from 80 to 100% depending on unit (preproduction and production, location, operator), with good correlation to compared methods, including laboratory and field data. Some differences noted; additional evaluations are needed.	Method[464] Field[129,130,465] (Thermal Electron Corp.)

Table 6. (cont.)

Measurement Method	Basis of Measurement	Methods Used for Comparability Tests (considered reference sampler*)	Qualitative Summary of Comparability Findings (details are provided in cited references)	Comments/References (vendor used in study)
		PHYSICAL PROPERTIES OF PM (cont.)		
CHEMICAL COMPOSITION OF PM (cont.)				
ANION AND CATION MONITORING (cont.)				
Methods Based on Analysis by IC				
PILS-IC	Following an inlet and a set of diffusion denuders to remove interfering gases, particles are grown by steam condensation with impaction onto a small spot on a glass wall that is flushed continuously with 0.1-mL/min purified water. PILS effluent is then transferred to a dual-column IC for anion and cation analysis with a 10-min cycle time.	Field tests (1999 Atlanta) SJAC PPD sampler ICVS ARA Denuder, filter-based* (New York: urban and rural) Denuder, filter-based* AMS R&P 8400S R&P 8400N Thermo Electron/Harvard	Atlanta: agreement of 20–35% for nitrate and 10–15% for sulfate among the continuous methods. Excellent agreement was observed in New York where slopes were close to 1 and $r^2 > 0.9$ among the continuous methods for sulfate. Recovery compared to filter-based methods was slightly lower (85% for continuous filter with $r^2 > 0.85$). In a second New York study, the PILS-IC was low by 28% in the urban area and 7% high in the rural area compared with filter-based measurements by the state of New York but highly correlated ($r^2 > 0.9$), although data completeness was low (~65–70%) because of operational problems with this initial commercial instrument. Good comparisons were obtained relative to the AMS for sulfate and nitrate; slopes reasonably close to 1 (within 30%) and $r^2 > 0.9$.	Method[123,124,466] Laboratory[123,466] Field[123,124,127,129,466] (Applikon Analytical, The Netherlands)
PILS-WSOC	PILS effluent collected as described above. PILS sample is transferred to a TOC analyzer to provide continuous 6-min integral measurements with a detection limit of 0.1 $\mu g/m^3$.	Field tests Filter-based	24-hr average PILS-WSOC data was compared to extracts from daily filters; regression slope was 1.35, $r^2 = 0.71$. Possible reasons for the higher WSOC values were suggested; additional evaluations are needed.	Method[133] Field[133] Results seem to correlate with high ozone events suggesting a correlation of WSOC with SOA, thus providing additional source-related information.
SJAC (MARGA)	Uses a rotating wet denuder to remove interfering gases, particles are then rapidly grown to 2 μm or larger in a steam condenser and collected by a cyclone with a 2-μm cutpoint. Collected liquid is pumped to an IC where it is analyzed for anion and cation species with a 15- to 200-min time resolution depending on desired detection limit. Method also used to estimate concentrations of gas-phase precursor species, such as HNO_3, NH_3, and HNO_2.[467]	Field tests (1999 Atlanta) PILS-IC PPD Sampler ICVS ARA Denuder, filter-based*	Agreement of 20–35% was obtained in Atlanta for nitrate and 10–15% for sulfate among the continuous methods. Tests in Europe and elsewhere also indicate excellent agreement with denuder filter-based methods and a thermo-denuder method with slopes close to 1 and $r^2 > 0.9$.	Method[124,467–469] Field[124,468] MARGA was referred to as SJAC prior to commercialization. (Applikon Analytical, The Netherlands)

Table 6. (cont.)

Measurement Method	Basis of Measurement	Methods Used for Comparability Tests (considered reference sampler*)	Qualitative Summary of Comparability Findings (details are provided in cited references)	Comments/References (vendor used in study)
		PHYSICAL PROPERTIES OF PM (cont.)		
CHEMICAL COMPOSITION OF PM (cont.)				
ANION AND CATION MONITORING (cont.)				
PPD sampler	Uses a PPD sampler to remove interfering gases, aerosol is then collected on one or two prewashed glass fiber filters that are automatically washed with water, solute is analyzed by IC for anions and cations with a 10-min time resolution. Gas-phase species can be obtained as well.	Field tests (1999 Atlanta) PILS-IC SJAC ICVS ARA Denuder, filter-based*	Agreement of 20–35% was obtained in Atlanta for nitrate and 10–15% for sulfate among the continuous methods. Gas-phase species (HNO_3 and HNO_2) were also measured in Atlanta with reasonable agreement to filter-based methods and SJAC.	Method[467,470] Field[124] (Dionex Corporation)
MAJOR CARBON COMPONENTS				
OC-EC Based on Thermal Optical Methods				
Sunset OC/EC	Sample collection on clean quartz-fiber filter after removal of interfering gas-phase species by a parallel plate charcoal-impregnated filter denuder.[471] Analysis by thermal evolution first in helium for OC and then in helium/2% oxygen for EC with multiple thermal steps and optical correction for charring; TC is the sum of OC and EC, time resolution is 1–2 hr.	Field tests Denuder/quartz-fiber filter methods* PC-BOSS	High precision obtained between collocated Sunset analyzers (OC $r^2 = 0.98$, EC $r^2 = 0.97$). Excellent agreement was obtained for TC in Lindon, UT, and Rubidoux, CA, with the PC-BOSS ($r^2 = 0.93$, slope = 0.90, intercept = 2 ± 2 $\mu g/m^3$). In St. Louis, 24-hr averaged continuous TC, OC, and EC agree well (TC $r^2 = 0.89$, slope = 0.97; OC $r^2 = 0.90$, slope = 0.93; EC $r^2 = 0.60$, slope = 0.95) with filter-based methods—the lower correlation for EC was likely due to low EC concentrations (0.7 $\mu g/m^3$ on average) with many EC values near or below the detection limit for the method. Comparisons by EPA in Chicago, IL; Seattle, WA; and Phoenix, AZ, also showed good agreement for OC, EC, and TC by the Sunset monitor, although stringent slope, r^2, and intercept criteria were only met part of the time.	Method[136] Field[33,136,137,462] Similar to laboratory analysis method (STN/NIOSH) used for EPA's National Chemical Speciation Monitoring Network. (Sunset Laboratory Inc.)
R&P 5400	$PM_{2.5}$ is collected on a stainless steel impactor maintained at 50 °C after larger particles are removed by a cyclone. Thermal evolution in helium/oxygen, first at 275 °C (or 340 °C) for OC and then 750 °C for TC. No optical correction for charring, EC by difference (TC − OC). Time resolution is 0.5–3 hr.	Field tests (RTP, NC and Fresno, CA) RAAS speciation sampler (quartz filter—TOT analysis) Aethalometer BC	In RTP, only moderate correlations were observed for TC and OC ($r^2 = 0.64$ and 0.67, respectively) between RAAS and R&P 5400 (5400), the 5400 underestimated TC and OC by 64% and 78% relative to RAAS. EC was overestimated by 5400 (89%); 5400 overestimated Aethalometer BC by 17%. In Fresno, the 5400 compared with TOR analysis of quartz-fiber filters overestimated TC by 40–60% and TC, OC, and EC were only moderately correlated ($r^2 = 0.4$–0.6). Operational problems were encountered with only 60% data capture in Fresno.	Method[132] Field[140,141] UF PM EC is measured by difference in a dual channel 5400, one side with a 0.14-μm impactor the other with a quartz-filter to measure total $PM_{2.5}$ EC.[472] The R&P 5400 is no long for sale by R&P (Thermo Fisher Scientific Inc.) (R&P)
SVOC (Sunset)	$PM_{2.5}$ OC is collected on a charcoal-impregnated glass fiber filter downstream of charcoal-impregnated cellulose filter denuder and quartz filter; 45-min collection followed by thermal evolution analysis and 1-hr time resolution.	Field test (Lindon, UT, February 2003; Rubidoux, CA, July 2003) PC-BOSS*	Nonvolatile (conventional Sunset), semi-volatile (modified Sunset), total OM was compared to respective species by PC-BOSS; r^2 close to or above 0.9, slopes close to 1.	Method[532] Field[532] In Rubidoux during July SVOC averaged 21% of the $PM_{2.5}$ mass as obtained by an FDMS-TEOM[33]

Table 6. (cont.)

Measurement Method	Basis of Measurement	Methods Used for Comparability Tests (considered reference sampler*)	Qualitative Summary of Comparability Findings (details are provided in cited references)	Comments/References (vendor used in study)
		PHYSICAL PROPERTIES OF PM (cont.)		
CHEMICAL COMPOSITION OF PM (cont.)				
BC Based on Absorption Methods				
Aethalometer	Continuously measures absorption of particles collected on a quartz-fiber filter tape at a specified wavelength (single, dual, and seven-wavelength systems are available). After transmittance reaches a preset lower level, the tape advances and the new filter spot is the initial blank for the measurement. Absorption is related to BC by an empirically defined calibration factor or absorption coefficient (m^2/g), which varies depending on wavelength used and physical and chemical properties of the aerosol. Default value in commercial Aethalometer is 16.6 m^2/g.	Laboratory Modeled absorption and scattering Field tests (Multiple locations) RAAS EC by TOT RAAS EC by TOR R&P 5400 PAS	Comparison of Aethalometer BC to filter-based methods yielded significantly different results most likely depending on the TOA analysis protocol used for analyzing quartz-fiber filters. For TOT analysis, Aethalometer BC correlated well ($r^2 = 0.86$) with the RAAS EC but Aethalometer BC overestimated RAAS EC by 30%. For TOR analysis, Aethalometer BC underestimated RAAS EC by 25% but was well correlated. Comparison with the R&P 5400 was similar to the TOT analysis with R&P 5400 EC greater than BC by 17%. PAS and filter-based methods agreed to about 15%.	Method[142] Laboratory[144,146] Field[140,141,144–146,198,473] (Magee Scientific Co.)
PAS	Air is drawn into an acoustic cell after having NO_2 removed. The sample is illuminated by light at a specified wavelength modulated at the resonant frequency of the cell. The absorbing aerosol is heated and cooled, which develops a pressure variation in the carrier gas that is effectively a sound wave, the intensity of which can be measured with a microphone. Concentration of BC in the cell is proportional to the sound intensity.	Laboratory tests Calibration with NO_2; tested with kerosene-flame soot, diesel soot, and spark-generated aerosol Field tests Thermal optical methods Aethalometer PSAP	Laboratory calibration with NO_2 compared well with absorption theory. Evaluation of generated aerosol lead to better understanding of absorption process and correction factors. PAS BC compared with TOA EC agreed to within ~15%. TOR EC yielded high correlations ($r^2 > 0.9$, 0.85) with slopes of 5–10 m^2/g and 3.6 m^2/g, respectively. In southeast Texas and Reno, NV, slopes between 8.1 and 8.4 m^2/g were observed. PSAP yielded high correlations but PSAP values were greater by 1.6. Several studies indicated the wavelength dependence of absorption by aerosols.	Method[143,148] Laboratory[146,473] Field[24,146,149,150]
TRACE ELEMENTS				
SEAS	Particles as small as 80 nm are grown by condensational growth from direct steam injection to > 3 μm. Particles are concentrated by a factor of about 7 by virtual impaction and separated from the air stream by real impaction. Samples are collected in vials for 30-min sampling periods. Collected slurry is analyzed in laboratory by GFAAS or by ICP-MS.	Laboratory PSL to evaluate system collection efficiency Field tests Limited compared to 24-hr average R&P dichotomous sampler filters analyzed by XRF	Collection efficiency is >80% for particles <1 μm. Agreement within 1 or 2 SD of the analytical precision was obtained for comparison to 24-hr average filter-XRF measurements for most of the elements. Differences in inlet cutpoints (1.2 vs. 2.5 μm) likely caused larger differences for normally PM_c species such as Al.	Method[153,156] Laboratory[153,156] Field[156] (OEI)

Table 6. (cont.)

Measurement Method	Basis of Measurement	Methods Used for Comparability Tests (considered reference sampler*)	Qualitative Summary of Comparability Findings (details are provided in cited references)	Comments/References (vendor used in study)
		PHYSICAL PROPERTIES OF PM (cont.)		
CHEMICAL COMPOSITION OF PM (cont.)				
PARTICLE MASS SPECTROMETERS				
	Single-particle MS: Particles are directed into a vacuum chamber, sized, and single particles are ablated by a single laser pulse, ions are removed to a mass spectrometer (usually a time-of-flight mass spectrometer in more recently developed instruments). Results in general are not quantitative without comparison to other methods that measure particles by size and or composition. AMS: The AMS draws particles into a vacuum chamber where they are sized, but particles are then impacted and volatilized on a heated surface with the components ionized by electron impact. The ions are detected by quadrupole MS. AMS is now also using time-of-flight MS. Method is reasonably quantitative. Particle MS instruments differ by how they obtain single particles: sized, ionized, detected, and categorized. See Middlebrook et al.[159] for a summary of the methods as used in the 1999 Atlanta Supersites Project.[5]	Field test (1999 Atlanta) Four-particle MS collocated for 1 month (PALMS, RAMS-II, ATOFMS, and AMS) Semicontinuous methods MOUDI A detailed summary of the evaluations and uses of particle MS is beyond the scope of this summary; however, readers are encouraged to examine the numerous papers in the four Supersites Special issues,[12–15] papers within the special issues resulting from the 2005 AAAR PM Supersites Conference (Atlanta, GA, February),[16–19] and the Supersites Program Synthesis special issue.[374]	The 1999 Atlanta Supersites Project represented the first time multiple particle mass spectrometers were compared in the field. Results indicated that despite their many differences, the laser-based methods identified similar individual particle classifications, and their relative fractions among comparable sized particles were generally consistent. AMS results were relatively consistent and were highly correlated to semicontinuous methods ($r^2 = 0.93$). For other comparisons and results, refer to Supersites Special Issues[12–19,374] and other journal papers.	Method[114,158,159] Field[12–19,114,158,159,189,190] Particle mass spectrometers likely represent the single greatest advancement in PM methods technology in the last decade. Over 20 papers associated with the Supersites Program have been published or are in press on the basis of evaluations and applications of the AMS alone. Particle mass spectrometer units were evaluated during the 1999 Atlanta Supersites Project[159] and were evaluated and/or used to obtain information on aerosol formation, processing, and source-receptor relationships at the New York, Baltimore, Pittsburgh, St. Louis, and Fresno Supersites Projects.[12–15,24,149,150,153,156,159,374]

Notes: [a]Reprinted/modified (updated) with permission from Solomon and Sioutas.[413] [b]Nephelometers have been widely used in visibility studies as a surrogate for $PM_{2.5}$ mass by measuring the light scattering due to particles. Conversion to mass requires several assumptions and is most often done empirically on the basis of comparison to filter-based gravimetric measurements; however, nephelometers were not used in Supersites Projects and are not reviewed in this paper. See McMurry[24] and references within for additional details. [c]McMurry[24] thoroughly reviews well-established methods for obtaining size distributions and total number concentration data by methods such as SMPS, APS, and CPC. Copyright 2006 Air & Waste Management Association, *Environmental Manager*. ARA = Atmospheric Research and Analysis, AIM = aerosol inorganics model, BAM = beta attenuation monitor, CAMM = continuous ambient mass monitor, cascade-ICVS = cascade impactor preceding the ICVS, ELPI = electrical low pressure impactor, GFEMN = Gibbs Free Energy Minimization Model, HI = Harvard impactor, IC = ion chromatography, ICVS = integrated collection and vaporization system, MARGA = monitor for aerosols and gasses in air, OEI = Ondov Enterprises, Inc., OPC = optical particle counter, PC-BOSS = Brigham Young University organic sampling system, PILS = particle-into-liquid sampler, PM_c BAM = PM_c measured using a BAM detector, PM_c TEOM = PM_c measured using a TEOM detector, PPD = parallel plate denuder sampler, PSAP = particle soot absorption photometer, PSL = polystyrene latex (particles), RTP = Research Triangle Park (North Carolina), SJAC = steam jet aerosol collector, TOT = thermal optical transmittance, UF PM BAM = UF PM measured using a BAM detector, URG MASS = University Research Glassware mass aerosol speciation sampler.

particles.[91] Results indicate that the D-TEOM and FDMS-TEOM likely provide the least biased measurements of ambient $PM_{2.5}$ mass relative to what is actually in the air,[30,31,33,34,92–95,533] and that the standard 50 °C TEOM is likely a good measure of nonvolatile PM.[29,33] These results strongly support the more widespread incorporation into routine mass monitoring networks of these continuous mass monitors, which are less influenced by sampling artifacts, once these samplers have been fully evaluated.[20] The new regulations promulgated in conjunction with the revised $PM_{2.5}$ NAAQS[96] will then permit these methods to gain Federal Equivalent Method (FEM) status, and thus be more widely used in regulatory and research networks. Such use will provide more complete $PM_{2.5}$ mass concentration data as well as input into Air Quality Index reports to alert the public to episodes of diminished particulate air quality. Health-related studies using these methods will be able to account for the health effects of semi-volatile components as well, because a fraction of these are not accounted for with the current standard filter-based methods that use Teflon filters.

Continuous monitors also were developed and evaluated to measure PM mass in the coarse particle size range (PM_c, AD between 2.5 and 10 μm)[97,98] and ultrafine particulate matter mass (UF PM, AD typically defined as <100 nm, but also defined as <150 nm because of limitations of the impaction methods used).[99] UF PM mass agreed well with the historical methods used for comparison. Importantly, the UF PM mass did not correlate with UF PM number concentration or with $PM_{2.5}$ mass, demonstrating the need to measure UF PM mass directly if this variable is deemed health relevant. The PM_c mass monitor was developed by the Los Angeles Supersites Project in conjunction with EPA's Office of Research and Development.[97,98] It underwent evaluation as a PM_c FEM, for use in an EPA PM_c monitoring network[100] in anticipation of a possible future PM NAAQS for PM_c.

Continuous indirect measurements of mass (UF PM, $PM_{2.5}$, PM_c) also were evaluated based on combined size distribution measurements made with a scanning mobility particle sizer (SMPS, 3- to 800-nm diameter particles) and an aerodynamic particle sizer (APS, 600 nm to 10 μm diameter particles). Size distributions can be converted to mass by applying shape and density factors, a desirable approach because particles are not collected on a filter and subject to typical filter-based sampling artifacts. Results indicate that reasonable agreement (±20%) can be obtained for $PM_{2.5}$ mass, but poor correlations are obtained for UF PM mass and PM_c mass[99,101–103] in agreement with other studies,[104–106] although Vanderpool et al.[100] indicated good agreement for PM_c mass compared with the APS.

Physical Properties. Development and evaluation of methods within the Supersites Program and related studies that measured the physical properties of PM focused on size distribution and number concentration, estimates of particle density, PBW, and particle morphology. A new water-based condensation particle counter (WCPC)[107,108] was developed that uses water rather than butanol to grow particles to a size at which they could be counted optically and it compared well to the butanol-based system.[109,110] Water as a condensation reagent is advantageous because condensation particle counter (CPC) instruments are often used indoors and butanol is flammable, toxic, and has a strong disagreeable odor.

Particle density is an important property of aerosols because it is required to convert measured number distributions to mass distributions, to relate AD to Stokes diameter,[24] and is crucial in determining where particles of a given size deposit in the respiratory system. Application of new approaches allows for continuous measurements of particle density by combining two of three methods that measure either mobility diameter, AD, or particle mass[24,111–113]; or by combining aerosol mass spectrometer (AMS[114]) and size distribution data;[115] and by comparison of size distribution data and continuous mass.[101,102] Data obtained in multiple locations indicate that $PM_{2.5}$, in general, has a density of approximately 1.5–1.7 gm/cm^3, which falls within the expected range for an aerosol composed mostly of sulfate, nitrate, and OC, and approximately 10% trace elements (e.g., Khlystov et al.[102]). Density data were also obtained for SOA formed from ozonolysis of α-pinene, β-pinene, and *d*-limonene.[116] Density was in the range of 1.4–1.65 g/cm^3 for most samples, but lower densities also were observed for two samples, suggesting changes in morphology that depend on SOA formation conditions.

For the first time, aerosol water content (μg/m^3) was measured continuously across the size range from 3 nm to 10 μm by a new method referred to as dry and ambient aerosol size spectrometry (DAASS).[117] In the past, particles of a given size (e.g., at 300 nm) were simply classified as less hygroscopic or more hygroscopic.[24,118] Using the DAASS data along with other continuous measurements collected simultaneously at the Pittsburgh Supersite, Rees et al.[90] were able to close the hourly average mass balance for $PM_{2.5}$ to within the measurement error of the methods. Results indicated that a greater amount of water was associated with the aerosol in the summer and that the highest water content occurred when the aerosol was acidic.[90,102] Khlystov et al.[119] also indicated that in Pittsburgh, even drying the aerosol at 30% relative humidity (RH) does not fully remove PBW from the particles in the summer.

Particle morphology was examined at the Baltimore Supersites Project for $PM_{2.5}$ during November 2002.[120] Size-fractionated samples (cut-off diameters of 0.10, 0.15, 0.55, and 2 μm) using a low-pressure impactor were collected during four 1-hr sampling periods (morning, midday, early evening, and late evening) for 5 days. Transmission electron microscopy was used to obtain perimeter fractal dimensions for each particle border examined. Particle morphology relates to surface area and particle density, and thus may suggest influences on PM health effects and particle chemistry, among other issues. Results indicated that at the near-roadway site in Baltimore, particles below 0.15 μm had the highest fractal dimensions relative to the other size ranges. Particles in the 2-μm size range based on cut-off dimensions of the impactor were typically round in shape and had a fractal dimension close to 1. Higher fractal dimensions also were observed during the morning sampling period, and this was particularly pronounced for particles in the 0.15-μm size range. At night, particles were mostly round in shape. Particle less than 50 nm were also typically round in shape at night.

Chemical Composition. Major components of $PM_{2.5}$ include sulfate, nitrate, ammonium, OC, EC, and crustal material, often defined as the sum of several trace metals based on their common oxides. Many evaluations of continuous methods to measure the chemical components of PM in near-real time were performed during the Supersites Program, as described in the next four sections.

(1) Anions and Cations: Two general approaches to measuring anions and cations continuously in PM were evaluated during the Supersites Program (see Table 6): (1) thermal reduction and detection with gas analyzers (TR-GA);[121,122] and (2) particle growth by condensation, followed by impaction, and analysis by ion chromatography (IC).[123] The TR-GA methods are indirect methods and often underestimated, by as much as 40%, their target species relative to time-integrated filter-based methods.[32,33,124–130] Although nonlinear, a reasonable correlation using the daily filter-based methods as a basis allowed calibration of 24-hr average continuous data to daily data with subsequent use of hourly data, although calibration to filter-based data are required to obtain suitable results (e.g., Wittig et al.,[125] Harrison et al.[126]). Frequent operational problems, frequent maintenance, and required operation by trained personnel were encountered.[125,128,130]

IC-based methods directly measured anions or cations of interest and appear to compare better to filter-based methods than the indirect methods,[33,124,129] although they still require a reasonable amount of attention to operate successfully in the field.

(2) OC, EC, and Black Carbon: Two continuous instruments have been developed and are commercially available to simultaneously measure the major components of particulate carbon in air, EC, OC, and total carbon (TC, equal to the sum of OC and EC) (see Table 6). One is a thermal-optical method based on the off-line NIOSH laboratory analysis approach[43,113] (Sunset Laboratory), and the other is a thermal only method (Model 5400, Rupprecht & Patashnick Co. [R&P], Inc., now Thermo Fisher Scientific, Inc.).[132] Thermo Fisher Scientific has discontinued the Model 5400, although its comparisons are included in this synthesis because it was evaluated thoroughly through the Supersites Program. A third instrument provides estimates of water-soluble OC (WSOC).[133] Addition of an XAD-8 resin column to the system allowed for measurements of hydrophobic and hydrophilic fractions[134] as well as speciation into acid, neutral, and basic fractions.[135] Continuous methods for determining black carbon (BC) on the basis of an absorption measurement in units of 1/m that can be converted to ambient concentrations in $\mu g/m^3$ by applying an absorption coefficient (m^2/g) also have been evaluated. These instruments include the Aethalometer, the photoacoustic spectrometer (PAS), and multi-angle absorption photometer (MAAP).

Results indicate excellent agreement for OC, EC, and TC by the Sunset method when similar filter-based methods are used for comparison;[136–138] with greater uncertainty if the filter-based analysis method differs from that used in the Sunset monitor.[139] The R&P 5400 shows inconsistent results compared with the filter-based methods, in part because of the differences between the R&P 5400 and the different filter-based methods used.[138,140,141] Similar to the filter-based methods discussed above, the measurement results indicate the effect different analysis protocols have on the OC and EC split, and consequently, on their reported concentrations. No comparisons were conducted to date to evaluate the WSOC method. However, the reported results suggest that at times, WSOC is a reasonable surrogate for the SOA mass.[133]

BC measured by the Aethalometer[142] or PAS[143] is an optically defined measurement similar to but different than EC, which is thermally defined.[20,25] BC is a key variable relevant to understanding the Earth's radiation budget and global warming. Following Beers Law, an empirically defined absorption coefficient (m^2/g) is used to convert absorption (1/m) to ambient concentration (units of $\mu g/m^3$). However, the absorption coefficient varies depending on the absorption wavelength, the physical and chemical properties of the aerosol, and the EC calibration method.[144–146] Thus, the Aethalometer requires calibration as a function of sampling location, possibly season, and the method used for calibration of the absorption coefficient. Furthermore, the absorption coefficient might be nonlinear throughout the absorbance range of interest.[138–140,147]

PAS[143,148] measures the in situ absorption (b_{abs}) of particles in air and avoids common interferences associated with collection of carbonaceous material on filters. PAS can be calibrated using nitrogen dioxide (NO_2), which cannot be done with filter-based methods or the Aethalometer, so uncertainty can be better defined. Comparisons with the Aethalometer and filter-based methods are usually well correlated, although the results are wavelength dependent, relying on the absorption coefficient (m^2/g) chosen to convert from absorption (units 1/m) to ambient concentrations ($\mu g/m^3$).[24,149,150] PAS appears to be the best available technique for measuring particle absorption, and although great progress has been made recently in understanding the method, more work is needed before it is suitable for routine regulatory monitoring.[20]

The MAAP measures light reflected from the filter at 130° and 165° from the illumination direction, which is subsequently used in radiative transfer models to estimate b_{abs}, which can be converted to BC.[151] This unit was compared with other BC and EC methods during a 1-yr period at the Fresno Supersite. The other continuous methods included the two- and seven-wavelength Aethalometer, PAS measuring PAHs, the Sunset continuous carbon analyzer, and the R&P 5400 carbon analyzer. These continuous methods also were compared with 24-hr average EC obtained by the IMPROVE thermal/optical reflectance (TOR) method from integrated filter samples.[139] Results indicated that MAAP BC, seven-wavelength Aethalometer BC, Sunset optical BC, Sunset thermal EC, and PAH values were highly correlated in winter ($r > 0.9$). However, although the intercepts were well within 1 $\mu g/m^3$, the slopes varied from unity to about a factor of 2, again indicating the continuing problem of relating light absorbance (BC) to EC mass in $\mu g/m^3$.

(3) Organic Species: Within the Supersites Program, the highest time resolution measurements of organic species were obtained using an integrated filter-based sampler operated at the Baltimore Supersite as described above.[66]

Recently, Williams et al.[152] reported on a continuous method for the determination of individual organic species at high-time resolution (1 hr or less) based on thermal desorption aerosol GC/MS-flame ionization detection (FID). The instrument was tested for 1 day in January 2004 at the University of California–Berkeley. Fifteen 1-hr samples were collected and approximately 100 organic species were identified. Limited factor analysis identified three factors. One factor associated with wood smoke (e.g., levoglucosan and other relevant wood burning markers), one factor associated with anthropogenic combustion and/or biogenic sources (e.g., alkanes, including an odd-carbon abundance at C27–C32), and the last factor associated with photochemical processes (e.g., oxygenated compounds—keytones, aldehydes, and alcohols—correlated with this last factor).

(4) Trace Elements: Methods are not currently available for the continuous measurement of trace elements in the field. However, high-time-resolution $PM_{2.5}$ data are being obtained for up to 12 trace elements by the Semicontinuous Elements in Aerosol Sampler (SEAS).[153–156] An improved instrument, SEAS-II, was deployed at three Supersites Projects. The particles are grown by condensation of water vapor as they pass through a long, cooled, glass-walled condenser at a flow rate of approximately 90 L/min with collection into sample vials that are switched every 30 min. Up to 48 samples can be collected in 1 day. The collected solutions were subsequently analyzed in the laboratory by graphite furnace atomic absorption spectrometry (GFAAS) for 10–12 trace elements that are important tracers for source apportionment modeling (e.g., aluminum [Al], arsenic [As], cadmium [Cd], chromium [Cr], copper [Cu], iron [Fe], magnesium [Mn], nickel [Ni], lead [Pb], antimony [Sb], selenium [Se], and Zn). Multielement electrothermal atomic absorption spectrometry (ETAAS) also was used and compared with instrumental neutron activation analysis (INAA) with very good agreement for most elements measured. The analytical methods were evaluated by comparison to NIST rainwater and NIST urban PM.[153–155] Good agreement was observed for most trace elements measured in rainwater (NIST SRM 1643; SRM 1640) and urban PM (NIST SRM 1648) and the NIST interim $PM_{2.5}$ reference material, although recoveries for some elements in PM were lower than NIST values. Pancras et al.[156] compared results from the SEAS-II to trace elements measured by X-ray fluorescence (XRF) for $PM_{2.5}$ collected on Teflon filters. Although the uncertainty for XRF was poorer for most elements, in general, agreement was within 2σ of the precision of the methods. Applications of these data are proving to be very useful in not only identifying specific sources, but also obtaining emissions rates from those sources as well. The latter has been achieved through the development and application of a new model that combines receptor modeling with Gaussian plume modeling and comparably time-resolved meteorological data.[156,157] The model is discussed later in this paper.

Particle Mass Spectrometers. Significant progress has taken place in the development and application of particle mass spectrometers during the last decade.[114,158] In particular, much progress has occurred since 1999 when, during the Atlanta Supersites Experiment,[5] four particle mass spectrometers were compared for the first time[159] (see Table 6). Before this time, no intercomparisons had occurred. In fact, this was the first field deployment for all of the methods with the exception of the aerosol time-of-flight mass spectrometer (ATOFMS). Availability of numerous coincident continuous and filter-based methods in Atlanta provided a strong basis for diagnosing particle mass spectrometers' behavior. Middlebrook et al.[159] described differences among the instruments. In general, the different single-particle methods identified similar particle types with reasonable agreement among comparable size fractions.

Single-particle methods have advanced significantly since the 1999 Atlanta Supersites Project, becoming important measurement methods in the research community and likely representing the single greatest advance in PM measurement technologies during the last decade. Descriptions of the methods are beyond the scope of this paper; however, insights gained from particle mass spectrometers are described in two other recent reviews.[114,158] These papers show the extent of information being learned from application of these methods, most achieved just over the last few years. In addition, a number of papers published in the four dedicated Supersites Program special issues and the four special issues published as a result of the 2005 AAAR PM Supersites Meeting, all noted earlier, illustrate the importance of these methods and some of these results are highlighted in next section.

CHARACTERIZATION OF AMBIENT PM

Annual or Study Period and Daily Average $PM_{2.5}$ Mass

Annual or study period average mass concentrations are listed in Table 7a for all Phase II Supersite Projects. Study averages are presented for Baltimore (9 months) and Los Angeles (five locations at ~6–8 months each, with only Claremont operating for a continuous year). On the basis of these data, the level of the annual average $PM_{2.5}$ NAAQS (15 $\mu g/m^3$)[96] was exceeded during study periods at all sites except those in Houston. Although these data do not represent official regulatory data and may or may not indicate violations of the NAAQS because of the type or location of the monitors, they are based on various samplers (Table 7a) that include FRM and FRM-comparable instruments. Table 7b lists the absolute number of exceedances of the 24-hr average $PM_{2.5}$ NAAQS (65 $\mu g/m^3$, measured directly rather than as the 98th percentile),[96] and the new $PM_{2.5}$ NAAQS daily value (35 $\mu g/m^3$),[96,160] with the exception of Pittsburgh, which only reported the number of days that exceeded 50 $\mu g/m^3$. According to these data, exceedances of the 24-hr average 1997 $PM_{2.5}$ NAAQS occurred only once at the Baltimore Supersites Project, three times in Rubidoux, CA, and 23 times in Fresno. The Baltimore exceedance was due to a rare event from the impact of the Canadian fires during July 2002[161] that affected the entire mid-Atlantic and northeastern U.S. regions (Begum et al.[162] and Rao, V.[535]). As seen in Table 7b, all sites will exceed the new $PM_{2.5}$

Table 7a. Annual or study period average data.

	Concentrations ($\mu g/m^3$)[a]								
Time Period	**Atlanta[b]**	**New York[c]**	**Baltimore**	**Pittsburgh**	**St. Louis**	**Houston[d]**	**Fresno**	**Los Angeles[e]**	**Reference(s)**
1999 (March–December)	19.7–21.8								Butler et al.,[173]
2000 (January–December)	17.7–21.1								Russell[541]
2001 (January–December)	19.1–19.8								
2005 (January–December)	18.7–19.6								
2000 (January–December)		15.1/9.2/5.5							Schwab et al.,[34]
2001 (January–December)		13.9/15.6/8.1/7.0							Demerjian[542]
2002 (January–December)		12.8/14.2/10.1/6.8							
2003 (January–December)		13.5/14.8/9.3/5.7							
2004 (January–December)		12.2/13.7/9.1/6.1							
2005 (January–December)		12.2/13.8/9.9/6.8							
2001 (May–June)			19.0						Park et al.,[161]
2001 (July–August)			16.4						Ondov et
2002 (February–November)			16.9						al.[450]
2001–2003 (July–June)				15.5					Wittig et al.[175]
2001–2002 (May–April)					17.2[f]				Turner[539]
2002–2003 (May–April)					19.3[f]				
2002 (January–December)						9.9/12.2/12.3			Russell et al.,[178]
2003 (January–December)						12.0/13.2/14.0			Allen[543]
2004 (January–December)						12.1/12.5/13.5			
1999 (July–December)							30		Watson[544]
2000 (January–December)							22		
2001 (January–December)							25.7		
2002 (January–December)							22.9		
2003 (January–December)							18.4		
2004 (January–December)							16.4		
2005 (January–December)							15		
2001 (February–September)								25.2	Froines[545]
								39.0	
2001–2002								16.9	
(September–August)									
2003 (May–September)								17.5	

Notes: [a]Mass measured using: Atlanta—SES TEOM; Baltimore—SES TEOM; New York—Partisol FRM; Pittsburgh—SES TEOM; St. Louis—Harvard Impactor;[474] Houston, Fresno—Andersen single channel RAAS and FRM; Los Angeles—Partisol FRM. [b]Range over four sites from Assessment of Spatial Aerosol Composition in Atlanta (ASACA) study.[173] [c]Four locations were studied during the project. These included two urban locations in NYC: Queens College (PS219) and South Bronx (IS52); and two rural locations in New York State: Pinnacle State Park, Addison, NY (PSP) and Whiteface Mountain, Wilmington, NY (WFM). The reported values are in the respective order PS219/IS52/PSP/WFM. [d]Data listed are for Deer Park/Clinton (near HRM3)/Aldine. [e]Five locations were studied during the project. These included source locations in Downtown Los Angeles and Downey, and receptor locations in Claremont, Riverside, and Rubidoux. Dates at each location are as follows: Riverside: February–June 2001 (25.2 $\mu g/m^3$); Rubidoux: June–September 2001 (39.0 $\mu g/m^3$); Claremont (September 2001–August 2002); Downtown Los Angeles (May–September 2003); Downey (October–December 2000, not listed because of short duration at site). [f]2001–2002 would be 17.1 $\mu g/m^3$ excluding July 4, 2001, and 2002–2003 would be 18.8 $\mu g/m^3$ excluding July 4–5, 2003 when the site was impacted by microscale influences from a crowd setting off personal fireworks adjacent to the site.

NAAQS of 35 $\mu g/m^3$ multiple times, with significant variations likely from year to year as shown by sites with multiple years of data. Peak periods in the eastern United States occurred during the summer with occasional but high values also occurring in the fall. These high values were likely due to photochemically driven PM formation processes and long-range transport superimposing regional concentrations upon local PM levels in the summer. In the fall, these high values resulted from cooler temperatures that cause condensation of semi-volatile components, such as NH_4NO_3 and primary and secondary SVOC, while sufficient photochemistry is still occurring, and also from reduced mixing heights. In the eastern United States, the highest 24-hr values range from approximately 50 $\mu g/m^3$ to greater than 85 $\mu g/m^3$, occurring in either July or September. The Canadian fires, as noted above, influenced the peak value in Baltimore. In Fresno, which is not representative of all urban areas in the western United States, the peak concentration measured was greater than 170 $\mu g/m^3$, and values greater than either 65 or 35 $\mu g/m^3$ typically occurred in the late fall and winter. These peak values were due to high levels of NH_4NO_3 and primary OC, the latter from residential wood burning in the winter, as well as motor vehicle emissions. In Los Angeles, the peak 24-hr value occurred in Rubidoux, historically known for very high

Table 7b. Days exceeding standards.[a]

Location	Number of Days Exceeding 65 μg/m³[b]	Months and Year Occurred	Number of Days Exceeding 35 μg/m³[c]	Months and Year Occurred	Peak 24-hr Concentration (μg/m³)	Date of Peak Concentration	Reference(s)
Atlanta[d]							Russell[541]
1999	None		42	1999:January, June–December	48.5	September 2, 1999	
2005	None		23	2005: June–November.	62.9	July 25, 2005	
New York							Demerjian[542]
2000–2005	None		61 (IS52) 33 (PS219)[g]	Summer and winter	55.3	January 23, 2001	
Urban 2000–2005			17 (PSP)	Summer	45.9	June 23, 2002	
Rural	None		3 (WFM)				
Baltimore	1	July 2002	18	2002: June–December	85.7	July 7, 2002	Sapkota et al.,[475] Park et al.,[161] Adam et al.,[295] Pahlow et al.[229]
Pittsburgh	None		9 days exceeding 50 μg/m³	2001: July–August 2002: June–August	60.9	July 1, 2002	Wittig et al.[175]
St. Louis May 2001–April 2003[e]	None		29	2001: June–August, November 2002: June–December Most monthly exceedances (2–4) were in July–September 2002 (6 in July 2002)	48.7	September 9, 2002	Turner[539]
Houston 2002–2004							Russell et al.,[178] Allen[543]
Deer Park	None		None	None	24.8, 26.2, 30.4	2002, 2003, 2004	
Clinton	None		4, 1, 1	2002, 2003, 2004	56.2, 42.2, 44.8	2002, 2003, 2004	
Aldine	None		None	None	26.7, 31.0, 31.2	2002, 2003, 2004	
Fresno	23	1999: November–December; 2000: January, November–December; 2001: January, November; 2002: January-February, November; 2005: December	63	1999: October–December; 2000: January, November; 2001: January–March, November–December; 2002: January–February, November–December; 2003: January, November–December; 2004: January, October–November; 2005: January–March, November–December	170.7	January 1, 2001	Watson[544]
Los Angeles[f]		–	Not provided				Froines[545]
Downtown Los Angeles	None				49.7		
Claremont	None				40.3		
Riverside	3				82.8		
Rubidoux	None				35.2		

Notes: [a]Mass measured using: Atlanta—SES TEOM, New York—Partisol FRM, Urban (IS52 and PS219) and Rural (PSP and WFM), Baltimore—SES TEOM, Pittsburgh—SES TEOM, St. Louis—Harvard Impactor,[474] Fresno—information not provided with data, Los Angeles—Partisol FRM. [b]ref 1. [c]ref 96. [d]Jefferson Street, Assessment of Spatial Aerosol Composition in Atlanta (ASACA).[173] [e]Three exceedances on July 4, 2001 (70.1 μg/m³), July 4, 2002 (95.7 μg/m³), and July 5, 2002 (107.8 μg/m³) included when the site was impacted by microscale influences from a crowd setting off personal fireworks adjacent to the site. [f]Five locations were studied during the project. These included source locations in Downtown Los Angeles and Downey, and receptor locations in Claremont, Riverside, and Rubidoux. Dates at each location are as follows: Riverside: February–June 2001 (25.2 μg/m³); Rubidoux: June–September 2001 (39.0 μg/m³); Claremont: September 2001 to August 2002; Downtown Los Angeles: May–September 2003; Downey: October–December 2000 (not listed due to short duration at site). [g]PS219 = Queens College (urban location in NYC); IS52 = South Bronx (urban location in NYC); PSP = Pinnacle State Park, Addison, NY (rural New York location); WFM = Whiteface Mountain, Wilmington, NY (rural New York location).

levels of NH_4NO_3. These high levels result from NH_3 emitted in the eastern part of the air basin reacting with nitric acid (HNO_3) that formed as NO_x emissions transport from west to east across the Los Angeles Basin.

Temporal and Spatial Variability of Chemical Composition

Seasonal Variability. In general, PM chemical composition followed expected trends (e.g., Chu et al.,[163] Blanchard,[164] Vickery,[165] Demerjian and Mohnen,[166] and references that follow in this text) with OC, sulfate, nitrate, ammonium, EC, and trace elements (crustal-related elements) being the major components of $PM_{2.5}$ in all locations. Differences between sites and seasons were driven by meteorology (mixing heights, temperature, and RH, and thus physical processes and thermodynamics), emissions, atmospheric processing, and transport of PM at scales sometimes exceeding 1000 km. Seasonal variations of $PM_{2.5}$ were driven mostly by variations in secondary components: ammonium sulfate [$(NH_4)_2SO_4$], NH_4NO_3, and SOA, although at times, local primary emissions, particularly in urban areas, had a significant impact (e.g., residential wood combustion in Fresno in the winter). Sulfate was a predominant component in the eastern United States, especially in the summer and a minor component in the western United States year-round. Nitrate patterns contrasted with sulfate, especially in the western United States, although elevated eastern U.S. nitrate concentrations were observed during the winter. OC (primary plus secondary) was a fairly consistent and a major fraction of the $PM_{2.5}$ year round, accounting for 20–40% of the $PM_{2.5}$ mass, on average, at most locations. However, secondary OC tended to be higher in the summer whereas primary OC was higher in the winter.

In Fresno, $PM_{2.5}$ was identified as a wintertime problem, although high concentrations also are observed in the fall.[163,165,167,168] The major components during the winter in Fresno were primary OM and secondary NH_4NO_3. Secondary NH_4NO_3 was more regional, especially during wintertime PM episodes, whereas primary OC had a more distinct urban focus, especially in the winter during the evening,[169] suggesting an impact from residential wood combustion. SOA also accounted for up to 30% of the OC during wintertime episodes in the West.[163] In Fresno during the summer, O_3 was high, whereas sulfate was not.

In Los Angeles, accumulation-mode PM mass (0.1–2.5 μm) was lower in the winter than summer, mainly at receptor sites that were influenced by secondary aerosol formation in the summer.[77] In these aerosols, nitrate and OC were the major components with higher levels of nitrate observed in the eastern end of the basin at the receptor sites, as expected.[170–172] Thermodynamics also played a key role in defining the phase distribution of semi-volatile components. For example, PAH size distributions in Los Angeles depended on the volatility of the PAHs, with lower volatility PAH compounds partitioning into the condensed phase with decreasing temperature.[77]

At eastern U.S. locations, the aerosol was characterized by higher sulfate and significant amounts of SOA in the summer, when photochemical activity peaks, with higher overall OC (mostly primary), nitrate, and EC in the winter months because of lower mixing heights and cooler temperatures.[90,163,170,173–180] In Atlanta, the highest concentrations were observed in the summer, with sulfate typically being the largest contributor, although OC was typically the second most abundant species with a relatively flat seasonal trend.[163,173] OC consisted of primary and SOA with up to 46% of the OC being SOA.[147] Many particles observed during the summer of 1999 in Atlanta with the Particle Analysis by Laser Mass Spectrometry (PALMS) (0.35- to 2.5-μm size range) were internally mixed, virtually always with carbon and sulfate and they often contained other anions and cations, metals, and soot/hydrocarbons.[181]

In Pittsburgh, Rees et al.,[90] Tang et al.,[182] and Cabada et al.[177] reported that sulfate also was the largest component during the summer (>45% of $PM_{2.5}$ mass) because of long-range transport. During the winter, it dropped to 35%. Nitrate was a minor component in the summer (<3% on average) but approached 15% during the winter. OC had a relatively flat seasonal profile, ranging from 20% in the summer and winter to 30% in the fall, although higher values were observed in the summer of 2002[182] because of the influence of the Canadian fires.[162] During the summer in Pittsburgh, Cabada et al.[183] estimated that 35% (range of 20–50%) of the OC was secondary; however, the EC tracer method is sensitive to the analytical method used to determine OC and EC.[52,184–186] Millet et al.[187] also reported that on average 37% of the OC in the summer was secondary in Pittsburgh, whereas during winter only 15% of OC was secondary. Millet et al.[187] indicated that local automotive emissions were the strongest contributor to changes in atmospheric volatile organic compound (VOC) concentrations. However, VOCs did not significantly affect the ambient concentration of organic aerosol, indicating both long-range transport and primary local industrial emissions were more important sources of organic aerosol during the study period. EC also had a relatively flat diurnal profile. On the basis of hourly Pittsburgh Supersites data, Zhang et al.[115] indicated that the aerosol was often acidic during pollution episodes in the summer, with more than 50% in the form of ammonium bisulfate (NH_4HSO_4); however, no enhancement was observed in SOA with respect to particle acidity.

Sulfate also was the largest component in New York during the summer, at both urban and rural sites,[180,188–190] except at the Whiteface Mountain high elevation site, and was fairly uniform on average across the urban and rural sites. Sulfate showed a distinct summer maximum, whereas OC stayed within a narrow range on average. One exception was during July 2002 because of the impact of the Canadian fires, when seasonally averaged OC was higher by approximately 1 $\mu g/m^3$. Nitrate showed the typical peak in the winter with higher concentrations at urban than rural sites. In the winter, nitrate was about equal to sulfate and both were slightly higher than OC. EC and trace elements were highest at urban sites and showed little consistent seasonal trend.

Multi-day episodes in Baltimore,[161] typically occurring during the summer, were driven by OC, sulfate, or both. Although regional transport from distant source-intense regions (e.g., the Ohio River Valley) dominated

the highest episodes, short-term excursions because of primary emissions from local sources, such as morning traffic and stationary combustion sources, also influenced other episodes. In the late fall, during the second highest episode observed during the 9-month study (February–November 2002), nitrate also was a significant contributor, the result of cooler temperatures and higher RH. During periods with the highest O_3 concentrations, approximately 60% on average of the hourly OC in Baltimore was secondary, with a maximum of 82%.[191]

In southeast Texas, sulfate, carbon, and ammonium accounted for more than 71% of the $PM_{2.5}$ mass on average during the 2-yr study period from January 2000 to December 2001, with little spatial variation in the mean mass or mean composition, although considerable variability was observed on a daily basis.[178] Russell and Allen[179] indicated peak primary OC and EC occurred in the winter along with maximum concentrations of other primary pollutants. However, peak secondary OC occurred in September coincident with the highest O_3 concentrations. On average, maximum monthly primary and secondary OC contributed a similar fraction of approximately 10–20% each to the $PM_{2.5}$ mass.

As described above, maximum PM concentrations in the eastern United States occurred in the summer. These concentrations tended to peak during multi-day episodes in which a clean period of a few days to a week was followed by pollution buildup over several days, with rather quick removal at the end of the episode generally resulting from the passage of a frontal system.[5,39,40,90,115,124,161,192,193] Episodes in the eastern United States tended to have higher fractions of OC or sulfate than on average, depending on the pollutants driving the episode.[161] In Fresno, winter PM episodes can last for extended periods of time, and two 3-week episodes were described by Turkiewicz et al.[169] and a single wintertime episode by Watson and Chow.[194]

ROS are oxygen-containing species with a strong oxidizing ability and have been suggested as important agents in inducing adverse health effects.[195–197] ROS include compounds such as oxygen-containing free radicals (hydroxyl [OH], hydroperoxyl [HO_2], and organic peroxyl radicals [RO_2]), molecules like hydrogen peroxide (H_2O_2) and organic peroxides, and ions such as the hypochlorite ion (OCl^-) and the superoxide anion (O^{-2}). They are found in both the particle and gas phases of the atmospheric aerosol. Little is known about the concentrations of particle-bound ROS in air or their behavior in different locations and seasons.

ROS were determined in various size fractions ranging from 10 nm to 18 μm using a Micro-Orifice Uniform Deposit Impactor (MOUDI) and nano-MOUDI (MSP) during July 2003 in Rubidoux, CA,[198] and during January and early February 2004 in Flushing, NY.[199] ROS were determined quantitatively using dichlorofluorescin (DCFH), a nonfluorescent reagent that becomes fluorescent dichlorofluorescin (DCF) upon reaction with ROS. The method is highly sensitive (picomole levels).[200] In both Rubidoux and Flushing, particle-bound ROS concentrations had a moderate correlation with O_3, an indicator of photochemical reactivity. Secondary OC and HO_x (HO_x = OH + OH_2) also had moderate correlations with ROS in Flushing, where these additional species were measured. These results along with the diurnal pattern of ROS suggested photochemical activity as the main source of ROS. However, the lack of a better correlation with HO_x species suggested a decoupling of particle-bound ROS with gas-phase oxidants. Study period 3-hr average total ROS concentrations in the 10-nm to 18-μm size range expressed in terms of equivalent H_2O_2 concentrations were in the range from 1.06 to 1.34 nanomol/m^3, with the highest average concentrations observed during the day (12:00 p.m. to 3:00 p.m.) and lowest values at night (5:00 p.m to 12:00 a.m.). Smaller particles were observed to have higher ROS concentrations, especially particles in the 10- to 56-nm size range. Similar diurnal results were observed at Rubidoux, CA; however, average total ROS concentrations were in the range of 500–600 nanomoles/m^3.[198] The lower levels at Flushing were likely due to the lower photochemical activity in the winter, lower precursor species levels as winds were from the northwest where no major sources are present, and higher wind speeds resulting in greater dilution and shorter residence times.[199] At both locations, the highest levels were observed in the UF PM size range, with a more moderate peak at Rubidoux in the 1- to 2.5-μm size range.

Measurements of OH and HO_2 radicals (HO_x = OH + OH_2) were obtained during the winter (January and February 2004)[201] and summer (July 2001)[202,203] in New York City (NYC) and during the summer (July–August 2001) at Whiteface Mountain as part of the New York Supersites Project.[204] These radicals, measured by laser-induced fluorescence (LIF) at low pressure,[205] are key diagnostics for understanding formation processes and evaluating chemical mechanism behavior. On average, the maximum daytime mixing ratios were 0.05 parts per trillion by volume (pptv) ($1.4 \times 10^6/cm^3$) and 0.7 pptv for OH and OH_2, respectively. Summertime levels measured in 2001 in NYC were approximately 5 times higher than these wintertime levels. During the summer at Whiteface Mountain, average noontime maximum mixing ratios were 0.11 and 20 pptv for OH and OH_2, respectively. Median diurnal profiles of measured OH and OH_2 along with OH reactivity for summer and wintertime measurements in NYC are illustrated in Figure 1. Mixing ratios of these two reactive species were much higher during the summer when solar radiation and photochemistry were at their highest levels. Photolysis of nitrous acid (HNO_2) was the dominant calculated HO_x source during the daytime, whereas O_3 and alkenes were the dominant calculated source at night. In NYC, the main calculated HO_x removal sink was the reaction of OH with NO_2. At Whiteface Mountain, the dominant sink was self-reaction of HO_2.

Individual organic species were measured at several of the Supersites Program locations as described earlier. The primary use of these data has been for estimating source impacts (see *Estimating Source Contributions at Receptor Locations* below). Seasonal data for organic species have been published only for Pittsburgh, PA, Los Angeles, CA, and Potsdam, NY, the latter in a related studies effort. Summertime measurements were reported in Houston, TX, and Research Triangle Park, NC. Seasonal trends were affected by source strengths, meteorology, and reactivity

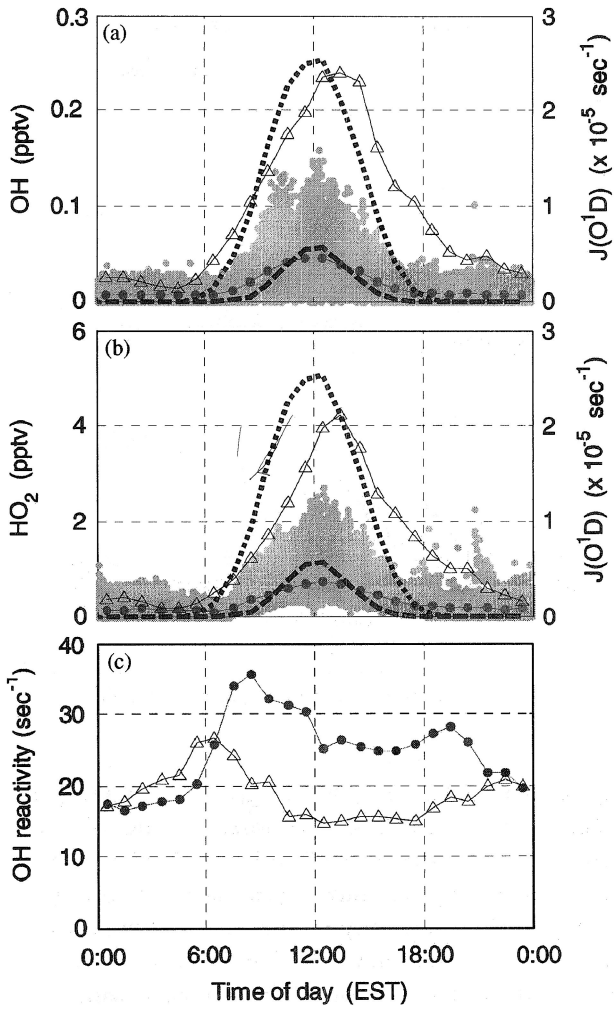


Figure 1. Median diurnal profiles of measured (a) OH, (b) HO_2, and (c) OH reactivity during the summer (from July 10 to August 2, 2001) and winter (from January 10 to February 6, 2004) campaigns in NYC, together with O_3 photolysis frequency, $J(O^1D)$. The small gray dots represent 1-min OH and HO_2 mixing ratios measured in the winter 2004 campaign. The solid gray circles show hourly median profiles in the winter campaign, and the triangles show the hourly median profiles in the summer campaign. The dashed line shows the wintertime $J(O^1D)$ and the dotted line shows the summertime $J(O^1D)$. Reprinted with permission from Ren et al.[201] Copyright 2006 Elsevier, *Atmospheric Environment*.

of the specific species. For example, SOA species or precursor gas or primary aerosol species with higher summertime emission rates tended to have higher concentrations in the summer, whereas certain primary species with higher emissions during the fall or winter (e.g., biomass burning tracers) had higher concentrations during those seasons. Of the species measured and reported to date in the literature resulting from the Supersites Program and related studies, those showing no distinctive seasonal pattern included cholesterol,[206] alkenoic acids (oleic and palmitoleic),[206] and hopanes (nonhopane and hopane).[206–208] Species exhibiting a distinctive summertime maximum included alkanoic acids (steric, palmitic, nonanoic),[206,207] hopanes (nonhopane and hopane) when normalized to EC to account for differences in atmospheric dilution,[207,208] semi-volatile PAHs,[77] 2-methyltetrols (2-methylthreitol and 2-methylerythritol), and *cis*-pinonic acid.[72] Species with highest concentrations in the fall or winter included levoglucosan,[72,209] resin acids and syringaldehyde,[209] and less volatile PAHs.[77]

Diurnal Variability. Widespread application of continuous species-specific methods during the Supersites Program allowed for detailed evaluation of diurnal variations of PM chemical components. Measurements at the Pittsburgh core sampling site,[125] indicated that during the summer, most of the nitrate was in the gas phase during the day and in the particulate phase during the night with maximum concentrations in the early morning before sunrise, similar to Atlanta.[124] In New York, essentially all available nitrate was in the particle phase in the winter. Sulfate concentrations showed little diurnal variation throughout the year, except in the summer, when sulfate peaked during the afternoon because of local photochemical production[210,211] as well as when downmixing occurred from long-range transport.[40] In Houston, mean diurnal patterns of $PM_{2.5}$ mass showed a consistent morning peak and a weaker and slightly less consistent late afternoon to early evening peak.[178] The afternoon peak was probably associated with biogenic SOA,[212] whereas the morning peak might have been due to a combination of a strong traffic source, low mixing heights, and early morning photochemical activity. However, the morning peak occurred at both urban and rural sites, sites near and far from roadways, and sites inland and near the coast.[178] In New York, on the basis of AMS data (<1 μm), mean sulfate concentrations showed a small afternoon peak, on average, during the summer of 2001, although this peak was strongly influenced by four multi-day episodes that were probably due to regional transport of pollutants and one episode in which local sulfate formation was important.[127] In Baltimore, as also observed elsewhere, nitrate had a strong diurnal pattern with peak concentrations occurring in the morning before or just after sunrise, likely associated with NO_x from morning traffic, and a minimum during the middle of the day with occasional nitrate peaks associated with photochemical activity.[161,213] A nighttime peak also was associated with particles in the PM_c size range. Morning and afternoon peaks were observed for OC, as noted previously, and likely driven by primary OC from motor vehicles in the morning and photochemical production in the afternoon.

Diurnal concentrations of 15 trace elements were obtained during the summer of 2001 and winter of 2004 at the New York Supersite in Queens using the Hi-flo (42 L/min) that allowed for the collection of 6-hr samples throughout the day.[39–41,192] Most of the trace elements peaked between 6:00 a.m. and 12:00 p.m., except Sb, which most often peaked between 12:00 a.m. and 6:00 a.m., likely from a local but unknown source.[40] Although not correlated, short-term, high concentrations of Pb and Sb were observed at various times throughout the study period. Comparison of species to a near-by site indicated homogeneous distributions for some species (Sb, cobalt [Co], vanadium [V], Se, and As) likely from distant sources based on the correlation between sulfate and Se and their link to distant coal-fired power plants, and heterogeneous

distributions from other species (Pb, Zn, Fe, Ni, Mn) likely affected by nearby sources. Trace metals were measured in $PM_{2.5}$ and PM_c at source (Downey, CA, September 2000–January 2001) and receptor (Riverside, CA, February–June 2001) locations in the Los Angeles Basin.[214] Samples were collected at each site four times per day to reflect morning traffic and midday, evening, and nighttime periods. Diurnal patters were different in the $PM_{2.5}$ and PM_c modes at each location with variations in PM_c metal concentrations driven by wind speed and $PM_{2.5}$ metal concentrations driven by meteorological conditions and source impacts.

UF PM samples were collected at an urban site during the summer in Los Angeles, CA.[215,216] Results indicated a peak in UF PM during the morning strongly associated with the morning commute and fresh motor vehicle emissions. An afternoon peak was associated with photochemical production through an increase in oxygenated organic acids and sulfate, whereas other species were diluted because of an increase in afternoon mixing height. UF PM peaked before O_3 possibly because of afternoon dilution and volatilization of the smallest particles with condensation onto larger particles. Three-hour averaged individual organic species concentrations were measured for the first time in ambient samples at the Baltimore Supersites Project.[64] With few exceptions, consistent diurnal concentration profiles were not observed with the individual organic species measured (Rogge measured 111 species, 18 days in the summer, 17 days in the winter). However, the averaged diurnal patterns (Figure 2) appear to follow the diurnal patterns of source activities. For example, hopanes (source markers for vehicular emissions) showed the highest average concentrations during early morning rush hour in the summer and winter. On the other hand, total PAHs minus phenanthrene had a relatively flat diurnal pattern in the summer indicating that local (e.g., motor vehicle) and distant sources (e.g., transport and photochemical activity) contribute to the ambient PAH concentrations. In wintertime, when meteorological conditions favor local sources, PAHs showed a diurnal concentration pattern that related to sources and activities generating PAHs locally (e.g., motor vehicle).

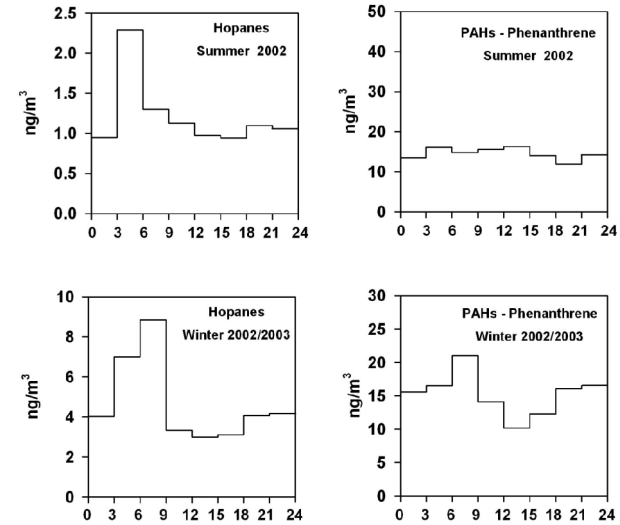


Figure 2. Time-integrated (3-hr sampling periods) concentrations of (a and c) hopanes and (b and d) PAHs (total PAH minus phenanthrene) for the summer and winter sampling periods measured at Ponca Street during the Baltimore Supersites Project. The x-axes show time (hour of day). Figure courtesy of W. Rogge, FIU, Miami, FL (now at University of California–Merced, Merced, CA).

Local and Regional PM

One of the main objectives of the Supersites Program was to support the implementation of the $PM_{2.5}$ NAAQS. These standards focus on urban air pollution where the greatest impact to human exposure and risk can occur. However, because transport can occur over 1000 km or more, regional or transported air pollution impacting urban areas can be important. In that regard, the following definitions of spatial scale typically have been used in the Supersites Program and this paper. The local or urban scale typically refers to a spatial distance of approximately 10–100 km (the size of a small to large urban area), whereas the regional scale refers to 100–1000 km, both as defined in the NARSTO PM assessment.[164] Smaller (neighborhood) and larger (continental and intercontinental) spatial scales also are defined in Blanchard.[164]

A significant fraction of the sulfate and OC in urban areas in the eastern United States is regional and transported into cities from upwind areas, although locally derived primary OC, EC, and other primary species also can be important contributors to $PM_{2.5}$ in urban areas, being superimposed on regional aerosol levels.[39,161,176–179,182,187–191,217–221] Spatial consistency for sulfate, ammonium, and OC at urban and rural sites in Pittsburgh and NYC indicate that a significant fraction of these species are regional and transported to these sites from upwind regions, especially during the summer. Primary species, such as EC and most trace elements, appear to be of local origin. Measurements at an upwind site and the central site in Pittsburgh indicated that approximately 90% of the sulfate at the Pittsburgh core site in July was because of transport from upwind areas.[177] These results were in general agreement with the estimates of Modey et al.[217] using measurements obtained at the National Energy and Technology Laboratory (NETL) outside of Pittsburgh and at the core site in Pittsburgh that showed high $PM_{2.5}$ episodes were generally associated with transport of pollutants during the transition from high pressure to low-pressure meteorological regimes. Measurements during the 2003 North American electrical blackout also indicated the impact of electric utility sources on regional PM and O_3 levels. Significant reductions were noted in regional levels of SO_2, O_3, and light scattering, but not carbon monoxide (CO) and light absorption based on aircraft measurements conducted in Pennsylvania during the middle of the blackout.[221]

Application of the Real-Time Single-Particle Mass Spectrometer III (RSMS III[222]) and AMS in Baltimore and Pittsburgh, respectively, permitted internally versus externally mixed particles to be distinguished from one another. Such separation can indicate the influence of secondary aerosols transported into the study area (internally mixed—two or more major components in

one particle) or primary locally derived particles (externally mixed—typically one major component in a particle).[115,193,219,223,224] Reported results typically included particles less than 1 μm with some distinction between the UF PM and accumulation modes. In general, particles greater than 100 nm were internally mixed containing carbon (including SOA), NH_4NO_3, and $(NH_4)_2SO_4$. Externally mixed particles, usually found in particles less than 10 nm included predominately only one major component, such as EC, NH_4NO_3, or transition/heavy metals believed to be of local origin. In the Pittsburgh area, aerosol residence times of 1–3 weeks were estimated based on measurements of radionuclides (^{210}Bi and ^{210}Po),[218] indicating that a significant fraction of the $PM_{2.5}$ observed in the Pittsburgh area was transported from outside of the area.

In Houston, monthly and annual average concentrations of $PM_{2.5}$ were relatively uniform throughout the area spatially, suggesting a regional influence on average. In contrast, daily observations indicated considerable spatial variability further influenced by high hourly or acute events, illustrating how local source impacts (e.g., from the industrial area of Houston) can be superimposed on regional PM levels.[178]

Daily measurements at an urban and two rural sites in New York indicated that sulfate concentrations were reasonably uniform over hundreds of kilometers, reaffirming the regional character of sulfate in the northeast.[39] On an annual basis, transport from upwind areas accounted for nearly 50% of the sulfate measured at the Queens urban site and approximately 60% at the rural and background sites, Pinnacle and Whiteface Mountain, respectively. Highest sulfate concentrations at all three sites were observed with air apparently transported from the Ohio River Valley and the Great Lakes Basin. In Queens, NY, during the summer of 2001, AMS (PM_1) and other continuous methods for $PM_{2.5}$ sulfate, nitrate, and OC, associated elevated $PM_{2.5}$ levels with local sources superimposed on the regional component.[188–190] Measurements in the winter also indicated an influence from regional transport with the highest PM levels occurring when southwesterly winds passed over the Ohio River Valley and southern Manhattan.[180]

Wildfires in both the eastern and the western United States can lead to high $PM_{2.5}$ concentrations.[63,191,193,225] The July 2002 forest fires in Quebec were responsible for significant increases in $PM_{2.5}$ mass levels throughout the East Coast of the United States to the point where several regulatory sites close to the daily $PM_{2.5}$ NAAQS at the time (65 $\mu g/m^3$) exceeded the standard because of the impact of the fires (Begum et al.,[162] Rao, V.[535]). The impact of the fires was observed at ground level at several mid-Atlantic sites, as well as the entire northeastern United States for several days in early July.[162] In Philadelphia, increases in ground-level concentrations of sulfate,[227] OC and EC,[145] and $PM_{2.5}$ mass, as well as O_3 and scattering coefficients by LIDAR (light detection and radar)[228] were observed because of the fires. Increases also were observed for $PM_{2.5}$ mass, OC, EC, and LIDAR aerosol backscatter in Baltimore,[191,229] whereas increases in OC and sulfate in Pittsburgh,[182,193] and mass, OC, and sulfate in NYC[41,188] were noted as a result of the Quebec fires. In Baltimore, the authors were able to provide reasonable source emissions estimates for OC and EC relative to those reported elsewhere and obtained by different methods as described later. In Pittsburgh, single-particle measurements of UF PM allowed distinction of (1) biomass particles from local sources on the basis of OC-to-EC ratios and the potassium (K) composition, and (2) relatively unprocessed particles from secondary composition by the presence of SOA and sulfate.[193] Aircraft measurements on July 8, 2002 over Virginia and Maryland showed two distinct layers: the Quebec smoke plume at 2–3 km above sea level and a plume from fossil fuel combustion below the smoke layer.[226] Large increases were observed within the smoke layer for submicron particle number concentrations, O_3, CO, scattering, and absorption, but not SO_2. Modeling results also confirmed the source of the smoke plume, its transport at 2–3 km above the surface, and the mechanism for bringing the plume to the surface.[230] The modeling results also agreed well with the measurement of optical properties by aircraft and remote sensing.

Measurements made within the Los Angeles Basin, during the Southern California wildfires in late October of 2003, indicated that much of the basin was impacted by the fires.[225] Of the pollutants measured, PM less than 10 μm in AD (PM_{10}) exhibited the greatest increase (a factor of 3–4) with a smaller impact observed for CO, nitric oxide (NO), and particle number (a factor of up to 2). NO_2 levels remained essentially unchanged and O_3 concentrations dropped during the fire episode, likely because of reduced levels of solar radiation. Particle size distributions of air sampled downwind of the fires showed number modes at diameters between 100 and 200 nm, significantly larger than that of typical urban air. Particles in this size range effectively penetrated indoors, possibly compromising the effectiveness of staying indoors to avoid exposure to wildfire emissions.

Major components and trace metals were measured in five size ranges at both source and receptor sites in Los Angeles, CA.[214] UF PM was dominated by carbonaceous material (~80–90%) at both sites with an OC-to-EC ratio of approximately 0.8–0.9. OC was the single largest contributor to each of the measured size ranges below 2.5 μm in Downey, whereas in Riverside, nitrate above 0.1 μm became the single largest component below 2.5 μm. Measured trace metals and elements were the largest component of PM_c in both locations (~55%). However, in Downey, a larger fraction of the remaining PM_c mass was OC, whereas in Riverside it was nitrate. Concentrations of trace metals in $PM_{2.5}$ were lower in Riverside than in Downey. Geller et al.[231] indicated that intermodal particles in the range from 1 to 2.5 μm are better correlated to PM_1 than to PM_c in both urban and rural locations. Therefore, the lower end of the PM_c size distribution (i.e., the lower tail) does not contribute significantly to the 1- to 2.5-μm size range in Los Angeles relative to the other components present and that much of the intermodal aerosol comes from submicron particle growth. Thus, in the greater Los Angeles area, a PM_1 standard would not provide a definitive separation between $PM_{2.5}$ and PM_c particles as suggested by others (e.g., Kegler et al.[232]).

Organic species were reported in several locations associated with the Supersites Program and related

studies, including Pittsburgh, PA; Research Triangle Park, NC; Houston, TX; Potsdam, NY; Los Angeles, CA; in the southeastern United States; and across the eastern United States. Ambient concentrations of specific organic species ranged from pg/m^3 to a few hundred ng/m^3 depending on the species, time of year, and location. Variations among regions were similar with noted differences; for example, levoglucosan concentrations were higher in Houston in the summer (study average of 234 ng/m^3),[63] whereas peak levels in the fall ranged from 5–70 ng/m^3 in Pittsburgh,[209] illustrating regional differences based on source strengths of this primary species. Cholesterol, alkenoic acids, alkanoic acids, hopanes, biomass markers (e.g., levoglucosan, resin acids), polar oxygenated compounds with one or more dicarboxylic acids and/or OH groups, 2-methyltetrols, and *n*-alkanes were in the range of about one to several hundred ng/m^3.[60,63,69,72,206–209,233,234] Quinones, hopanes, and the measured PAHs were in the pg/m^3 range (<10 to ~800 pg/m^3) on average.[63,71,77,235]

Fossil and Modern Carbon

OC in atmospheric aerosols consists of a combination of recently formed carbonaceous material (referred to in the literature as modern, biogenic, or contemporary carbon, although some distinction between these terms can be found; e.g., Hidy et al.[236]) and carbon derived from fossil fuel combustion. Thus, modern carbon has both natural and anthropogenic origins. The former is associated with recently living organisms (recent relative to fossil fuel carbon), and thus is derived from sources such as meat cooking, biomass burning, and noncombustion biogenic emissions including both gas-phase species (e.g., isoprene and various terpenes), which may be processed to form secondary OC, and primary biological particles (e.g., spores, pollens, plant waxes, etc.). Modern carbon contains the radioisotope ^{14}C in equilibrium with the current atmospheric concentration of $^{14}CO_2$ that formed from the interaction of cosmic rays with atmospheric nitrogen.[237] Modern carbon requires an adjustment because of the influence on ^{14}C from nuclear bomb testing. Fossil fuel carbon, on the other hand, is devoid of ^{14}C because carbon associated with fossil fuels greatly exceeds the half-life of ^{14}C (5730 yr). Fossil fuel carbon is essentially entirely anthropogenic, whereas modern carbon can be anthropogenic (e.g., residential wood burning) or natural (e.g., forest fires ignited by lightning). Thus, an important question in the apportionment of the carbonaceous aerosol is the relative amounts of fossil-fuel-derived carbon relative to modern carbon.

Table 8 summarizes results of percent modern carbon (pMC) determined at several Supersites Program and related study locations. A more complete listing is provided in the introduction of Lewis and Stiles.[238] Some of the first applications of the use of ^{14}C to identify fossil versus biogenic carbon sources were summarized by Currie et al.[239] and their results are included in Table 8 because they relate to two Supersites Program locations (Los Angeles and Houston). The only direct Supersites Program measurements were performed in Houston by Lemire et al.[212] They found that at an urban/suburban site 27–73% of the aerosol carbon was contemporary, whereas at a

Table 8. pMC[a] in $PM_{2.5}$: Summary at Supersites Program and related study locations.

City	Study Period	pMC[b] (%)	Comment	Reference
Los Angeles				
Durante	September 1979	0.52 ± 5 0.57 ± 4 0.85 ± 3	<1.7 μm AD 1.7–3.5 μm AD >3.5 μm AD	Curie et al.[239]
Long Beach (coastal), Azusa (inland)	1982 winter 1982 summer	Long Beach (33–43) Azusa (20–35) Modern carbon higher in the winter than summer because of wood smoke, a winter-only source.	Annual average; Source tests indicate wood smoke, meat cooking, paved road dust, cigarette smoke, and brake lining wear particles contribute 18 and 78% to pMC in Los Angeles.	Hildemann et al.[476]
Azusa	September 1997	7–34	VOC samples; varied by time of day.	Klouda et al.[477]
Denver, CO	December 1978	58 ± 12	$PM_{2.5}$	Curie et al.[239]
Houston, TX	September 1980	30 (range 10–60)	$PM_{2.5}$	Curie et al.[239]
	Summer 2002	Urban/suburban 27–73 Rural, forested 44–77	Sources are biomass burning and biogenic SOA.	Lemire et al.[212]
Nashville, TN	June–July 1999	56–80	$PM_{2.5}$, Chapman-Richard tree growth model applied. SOA determined by OC/EC ratio and it was highly related to pMC.	Lewis et al.[240]
Tampa, FL	May 2002	52–89	Corrected for OC filter positive artifact, small compared with total OC artifact (3% vs. 24%), SOA determined by OC/EC ratio and it was highly related to pMC.	Lewis and Stiles[238]
Look Rock, TN (Great Smoky Mountains National Park)	Spring/summer, 2000 Summer/fall, 2001	40–90	Rural/background site. pMC varied by season.	Tanner et al.[242]

Notes: [a]See references for exact calculations; [b]Results based on a limited number of samples at each location per study period.

rural forested site 44–77% of the carbon was contemporary. Analysis of emission inventories and related ambient measurements suggested that this modern carbon resulted from a combination of biomass burning and SOA formation from biogenic precursors.

Lewis et al.[240] introduced a new approach based on the Chapman-Richards model of tree growth to develop a quantitative relationship between measurements of the pMC and the percent of biogenic carbon, the latter being corrected for atmospheric nuclear weapons testing in the 1950s and early 1960s. In their Tampa, FL, study, Lewis and Stiles[238] examined the need to correct for positive OC sampling artifacts associated with quartz-fiber filters as discussed earlier in this paper. They found only a small correction was needed for pMC as compared with the total $PM_{2.5}$ OC artifact. For these summertime samples, Lewis and Stiles[238] estimated that a large portion (up to 79%) of the OC measured during the study must be SOA from biogenic VOC precursors. These results are similar to those observed during the summer in Nashville, TN, and southeastern Texas.[240] Results also indicate that biogenic sources significantly influence the OC content of atmospheric aerosols, even in urban areas such as Los Angeles,[239] where motor vehicles are assumed to be a dominant source of particulate carbon. The ^{14}C methods are useful, but analyses are costly and of limited use within routine networks.

SOAs

Primary and secondary particles can have both biogenic (natural) and anthropogenic (man-made) sources. In Houston, Yue and Fraser[63] and Vizuete et al.[241] showed how both biogenic and anthropogenic sources influence organic PM concentrations. The former analysis was based on measurements of nonpolar organic compounds in $PM_{2.5}$ that allowed distinction between biogenic plant waxes and fossil-fuel-derived organic components of the aerosol, whereas the latter research modeled sesquiterpene emissions data. Vizuete et al.[241] further showed that north and southwest of Houston, SOA formation is dominated by biogenic emission sources where forests emit large quantities of biogenic VOC. This is consistent with ^{14}C radiocarbon measurements by Lemire et al.,[212] in which biogenic SOA accounted for up to 80% of SOA north of Houston during the summer, whereas the fraction was significantly less and at times not detectable at urban locations. The urban Houston SOA is primarily anthropogenic because of industrial emissions of aromatic compounds. During one haze episode in Houston, agricultural burning and wildfires dominated the contribution of other $PM_{2.5}$ sources in the area.[63] At a rural site in Tennessee,[242] it was estimated that modern OC composed approximately 15–25% of the $PM_{2.5}$ mass, whereas fossil carbon comprised only approximately 13% of the $PM_{2.5}$ mass, with a significant fraction of the modern carbon resulting from plant emissions followed by photochemical oxidation. At times, agricultural and residential wood burning also affected the site. Other recent radiocarbon measurements also have indicated large contributions to OC from biogenic sources. Lewis and Stiles[238] and Lewis et al.[240] reported modern carbon contributions to OC ranging from approximately 50–90% in May 2002 (Tampa, FL) and June–July 1999 (Nashville, TN), respectively.

SOAs comprise a significant portion of the OC in the summer.[243] Recent efforts to characterize the species indicate SOAs are composed of oxygenated organic aerosols (OOAs) that correlate with other secondary species or other parameters that correlate with secondary species (high in the summer, middle of the day, etc.). For example, phthalic acid (1,2-benzenedicarboxylic acid) measurements in the southeastern United States were correlated with sulfate and nitrate.[60] In Los Angeles, CA, phthalic acids were correlated with the "other" mass in a chemical mass balance (CMB) apportionment model and found primarily in the accumulation mode, peaking in the daytime, and more prevalent in the summer, both relationships suggesting its origin was secondary.[62] Nitro-PAH species follow a similar temporal pattern to phthalic acid in Los Angeles.[244]

Ambient $PM_{2.5}$ filter samples collected in North Carolina were analyzed by FTIR to identify compound classes containing –C=O and –OH functional groups as well as by derivatization/MS to confirm the presence of the oxygenated species.[67] FTIR also was used in Houston to identify the presence of –C=O, –OH, organonitrates, and nitroaromatic compounds, suggesting a secondary origin for the submicron aerosol. These species also were observed in particles in the 1- to 4-μm size range in Houston, which may have resulted from unique plume chemistry occurring in plumes of industrial sources or because of unusual primary sources.[73] Yue and Fraser[233] measured a series of polar organic compounds in Houston, where diacids were suggested to be secondary aerosols. Other polar organic molecular markers appeared to be due to primary emission (levoglucosan—wood smoke; high molecular weight n-alkanoic acids (CPI >3), suggesting biogenic sources, such as plant waxes; *n*-alkenoic acids—meat cooking). Jaoui et al.[69] and Kleindienst et al.[70] identified and quantified a series of polar oxygenated compounds bearing one or more of each carboxylic and OH groups from oxidation of monoterpenes and toluene. They suggested these oxygenated species as possible atmospheric tracers for SOAs from monoterpenes and toluene oxidation. Studies by Claeys et al.[245] in the Amazonian rain forest and Edney et al.[246] in the eastern United States have suggested that the oxidation of isoprene can lead to 2-methyltetrols in $PM_{2.5}$. Recent field studies in a rural area of northern New York[72] and at urban and rural sites in the southeastern United States[247] have indicated that methyltetrols can represent up to 3% and up to 0.5%, respectively, of the OC associated with summertime concentrations of $PM_{2.5}$ mass. In New York, the concentrations fall to near zero during the winter. In Pittsburgh, a distinction between hydrocarbon-like aerosols (HOAs) and OOAs was interpreted from highly time-resolved organic mass spectra obtained with an AMS.[248,249] Results from approximately 2 weeks of measurements in September 2002 indicated that the HOA AMS spectra are similar to those of diesel exhaust, lubricating oil, and freshly emitted traffic aerosols observed in urban areas, whereas the OOA AMS spectra are similar to aged organic aerosols sampled in rural areas. HOA and OOA account for 34 and 66%, respectively, of the measured organic aerosol mass.

A recent review of data from 37 AMS field campaigns indicated that OOA is ubiquitous in atmospheric environments, on average accounting for 64, 83, and 95% of the total organic aerosol in urban, urban downwind, and rural/remote sites, respectively.[250]

The role of acidic seed particles in formation of SOA is currently uncertain, with chamber studies suggesting its potential importance (e.g., Gao et al.,[251] Jang et al.,[252,253]) but some field studies suggesting it may not be important in the atmosphere.[115,254] Hourly data collected in Pittsburgh indicated that the aerosol was often acidic during summertime pollution episodes with more than half of the sulfate in the form of NH_4HSO_4.[90,115] When acidic aerosol periods were compared with periods when the aerosol was neutral, using the hourly data, no coupling in the variations of organic aerosol and particle acidity was detected or relative enhancement in SOA concentrations. This suggests that the increases in SOA formation because of the presence of acidic aerosols, as noted in recent laboratory studies,[251–253] does not occur to an appreciable extent during the summer in Pittsburgh.[115,254] They estimated that even a drastic reduction of particle acidity in that area would not change the organic aerosol concentration by more than a few percent. Zhang et al.[255] also examined size-resolved AMS anion and cation data along with AMS OOA (a surrogate for SOA) and HOA (surrogate for primary organic aerosol) data and were unable to identify any distinct enhancement in SOA. In fact, the mass spectra ($m/z > 200$) of OOA during acidic and neutralized periods were almost identical, suggesting that the chemical nature of OOA is similar during the two periods and that no significant increase in SOA oligomer formation occurs in Pittsburgh when the aerosol is acidic. Tanner et al.,[256] also using hourly data collected across several research networks in the southeast United States, observed no enhancement in OC because of the presence of acidic aerosols. However, in Houston, measurements and modeling during a significant wood smoke episode, when the concentrations of acidic aerosols and SOA precursors occurred simultaneously, indicated possible SOA formation up to a few micrograms per cubic meter because of acid aerosol-mediated organic aerosol formation reactions that are not accounted for in most current photochemical models.[257] During pollution episodes at STN sites across the eastern United States, Chu et al.[163] reported similar aerosol acidity levels to those reported in Pittsburgh. However, on the basis of the 24-hr average STN data, their results suggested an enhancement in OC, even during a period of low photochemical activity, indicating the possible influence of acidic particles on SOA formation. It is possible that the use of 24-hr average data removes the diurnal variability differences between sulfate, OC, and acidity and the observed correlation is more influenced by meteorology rather than a causal relationship between particle acidity and enhanced SOA formation. This is similar to the advantages of using hourly data instead of daily averaged data in receptor modeling, which allows for a greater decoupling of the effect of meteorology on pollutant variability (see *Estimating of Source Contributions at Receptor Locations, Receptor-Oriented Approaches*). Thus, the influence of acidic seed particles in SOA formation is currently uncertain with chamber studies and 24-hr measurement data suggesting its potential importance but field studies using hourly data suggesting that it may not be important in the atmosphere, at least under the conditions tested.

Havers et al.[258] suggested that humic-like substances (HULIS) are important constituents of the OC associated with airborne PM. Kunit and Puxbaum[259] and Puxbaum and Tenze-Kunit[260] have reported on the presence of cellulose as a particulate organic component. These studies support the hypothesis that a large fraction of the organic aerosol is oligomeric or larger polymeric substances that are water-soluble and with unknown potential toxicity. It is uncertain whether these materials are primary or secondary in nature. However, recent evidence supports the concept of polymerization reactions that build oligomers from monomeric species in the atmosphere. Kalberer et al.[261] examined the organic components in smog-chamber experiments and found polymeric material with molecular masses up to around 1000 Da. Tolocka et al.[262] found oligomeric products between 200 and 900 Da. The masses and dissociation products of these ions were consistent with known primary products of reactions of monomers with and/or without the expected acid-catalyzed decomposition products of the monomers. Gao et al.[251] examined seven hydrocarbon systems (i.e., *r*-pinene, cyclohexene, 1-methyl cyclopentene, cycloheptene, 1-methyl cyclohexene, cyclooctene, and terpinolene) and observed oligomers with molecular weights from 250 to 1600 in the SOA formed, in both the absence and presence of seed particles and regardless of the seed particle acidity.

Thus, to ascertain how much of the OM in atmospheric aerosols is likely due to degraded primary biological material versus how much of it is because of secondary reaction products, there is a need to better understand both the role of aerosol acidity and the presence of HULIS and related materials in actual atmospheric aerosols. In addition, HULIS and terrestrial humic substances seem to have different chemical and physical properties so there is a need to understand better the composition of HULIS material to address these differences, both from atmospheric and health-effects sciences perspectives.[263]

UF PM

In the Supersites Program, the term UF PM was used primarily to define particles in the size range of less than 100 nm, as is typically found in the literature. However, because of restrictions by measurements methods, slightly larger upper particle ranges (up to ~150 nm) were included in the definition and are noted when used in the text.

The widespread use of single-particle MS or AMS during the Supersites Program has led to an unprecedented wealth of information on continuous particle composition by size for particles primarily below 1 μm at multiple locations impacted by a variety of sources and meteorological conditions. Information on UF PM is particularly unique to these data. In addition, at several sites size-fractionated samples were collected using a MOUDI,[264] providing composition and size-fractionated data from several hours to days. These data

were augmented by continuous size distribution or number concentration methods (e.g., SMPS, CPC). Locations where UF PM was extensively measured include Atlanta, New York, Baltimore, Pittsburgh, Houston, Fresno, and Los Angeles, although not all projects have published results to date. A few general statements can be made about UF PM aerosols on the basis of these measurements. First, UF PM varies considerably in composition, particle number concentration, and over space and time.[82,99,115,161,170,177,215,219,223,265–282] In virtually all locations, OC was a major fraction of the UF PM, except near industrial sources (e.g., Phares et al.[268]) and during nucleation events that occurred after sunrise on clean, sunny days in the eastern United States, where UF PM was initially dominated by sulfate.[278,283] Differences in the UF PM composition of the remaining significant fraction in which OC is the major constituent depend on location and typically include trace metals, EC, and nitrate.

Results from the RSMS II single-particle mass spectrometer measurements in Atlanta, GA,[269] and Houston, TX,[268] are illustrated Figure 3, a and b. Figure 3a clearly shows the dominance of OC in UF PM at urban sites not heavily influenced by industrial sources, although the impact of industrial and other sources at certain wind directions (WDs) are evident. In Houston (Figure 3b), industrial sources from all WDs strongly influenced the site, which was located just north of major industrial emissions sources. Carbon, although not a major component, is still observed in many of the pie charts. Sulfate was not detected by the RSMS II during these studies, but likely would only be present in particle sizes above a few hundred nanometers.

In Fresno, four types of UF PM events were observed: (1) 3- to 10-nm morning nucleation; (2) 10- to 30-nm morning traffic; (3) 10- to 30-nm afternoon photochemical; and (4) 50- to 84-nm evening home heating, including residential wood combustion.[282] These events varied between summer and winter and diurnally due to the impact of nucleation (likely initiated via H_2SO_4-NH_3-water) similar to the Pittsburgh events that occur in the morning after sunrise (type 1; described in more detail below), photochemical processing (type 2), and the impact of primary UF PM from traffic in the morning (type 3) and the impact of residential wood combustion in the evening (type 4). In Pittsburgh, UF PM composition varied between winter and summer.[177] In the summer, 50% of the UF PM aerosol was organic, and 40% was $(NH_4)_2SO_4$. In the winter, 70% appeared to be organic and only 25% $(NH_4)_2SO_4$, with minimal amounts of nitrate and crustal components. In addition, results from Los Angeles, indicated that UF PM composition can vary significantly within a given location, such as, between source areas and downwind receptor locations, only approximately 100 km away and within the same air basin.[277] Higher particle number concentrations were found in the winter compared with summer at Children's Health Study sites, with motor vehicle emissions having a greater impact in the winter. During the summer, higher number concentrations were associated with long-range transport often following a peak in O_3, which suggests new particle formation by photochemistry.[284]

Results in Los Angeles also indicate significant variations in UF PM number concentration with increasing distance from two freeways.[273–276] They compared results of a freeway dominated by gasoline vehicles to one with approximately 25% diesel vehicles and compared both during summer and winter periods (Figure 4, A and B). Modeled results indicate sulfuric acid-induced nucleation is the dominant particle production mechanism when gases exit the tailpipe, followed by the rapid condensation of organic compounds, resulting in the rapid growth of nuclei mode particles within 1–3 sec.[285] Dynamics driving aerosol size distributions and composition between the roadway to ambient environment (a few meters to 300 m) are dominated by condensation and dilution, whereas coagulation and deposition play minor roles.[285–287] Clearly, individuals living within 90 m of roadways are exposed to a unique size range of particles with varying composition that others are not.

Size distribution measurements of UF PM ($<\sim 100$ nm) made in conjunction with the Supersites Program and related studies (i.e., Southeastern Aerosol Research and Characterization Study [SEARCH][288] in Atlanta, GA; Rochester, NY; and Toronto, Canada) also indicate that UF PM exists in the atmosphere for extended periods of time.[103,265,266,278,279,289] In Pittsburgh,[278,279] homogeneous nucleation events or nucleation bursts were observed on approximately 50% of the study days with regionwide UF particle events on 30% of the study days. Regional events occurred after sunrise during mid- to late morning, lasted several hours, had number concentrations 3–10 times greater than days without nucleation, and occurred during all seasons, with winter being the least frequent. An example of the size distribution and growth during the day is illustrated in Figure 5 (lower plot). Events were observed on clean, sunny days at both the central urban and rural sites, although rural sites had number concentrations 2–3 times lower than the urban site because of the impact of local sources (motor vehicle traffic) at the urban site. AMS measurements in Pittsburgh by Zhang et al.[290] indicated that the regional nucleation events were initiated by formation of sulfuric acid (H_2SO_4) particles, followed within an hour by partial or full neutralization and initial growth by ammonium, followed by increases in OC during initial photochemical activity, with concurrent measurements of oxygenated species suggesting growth by addition of SOA (Figure 5, upper plot). Gaydos et al.[291] modeled these nucleation events, confirming that regional nucleation is a ternary process involving NH_3, H_2SO_4, and water. A second generation model, based in part on the model of Gaydos et al.[291] was developed and evaluated by Jung et al.[283] The model well reproduced the nucleation events from their start to completion.

Particle size distributions have been measured in Rochester, NY, since December 2001 with results similar to those observed at other eastern U.S. locations.[103,289] More than 70% of the measured total particle number concentration (number of particles per unit volume) was associated with UF PM (11–50 nm). Morning nucleation events, typically peaking in UF PM number concentrations at around 8:00 a.m. were apparent in winter months along with increased CO concentrations. These particles

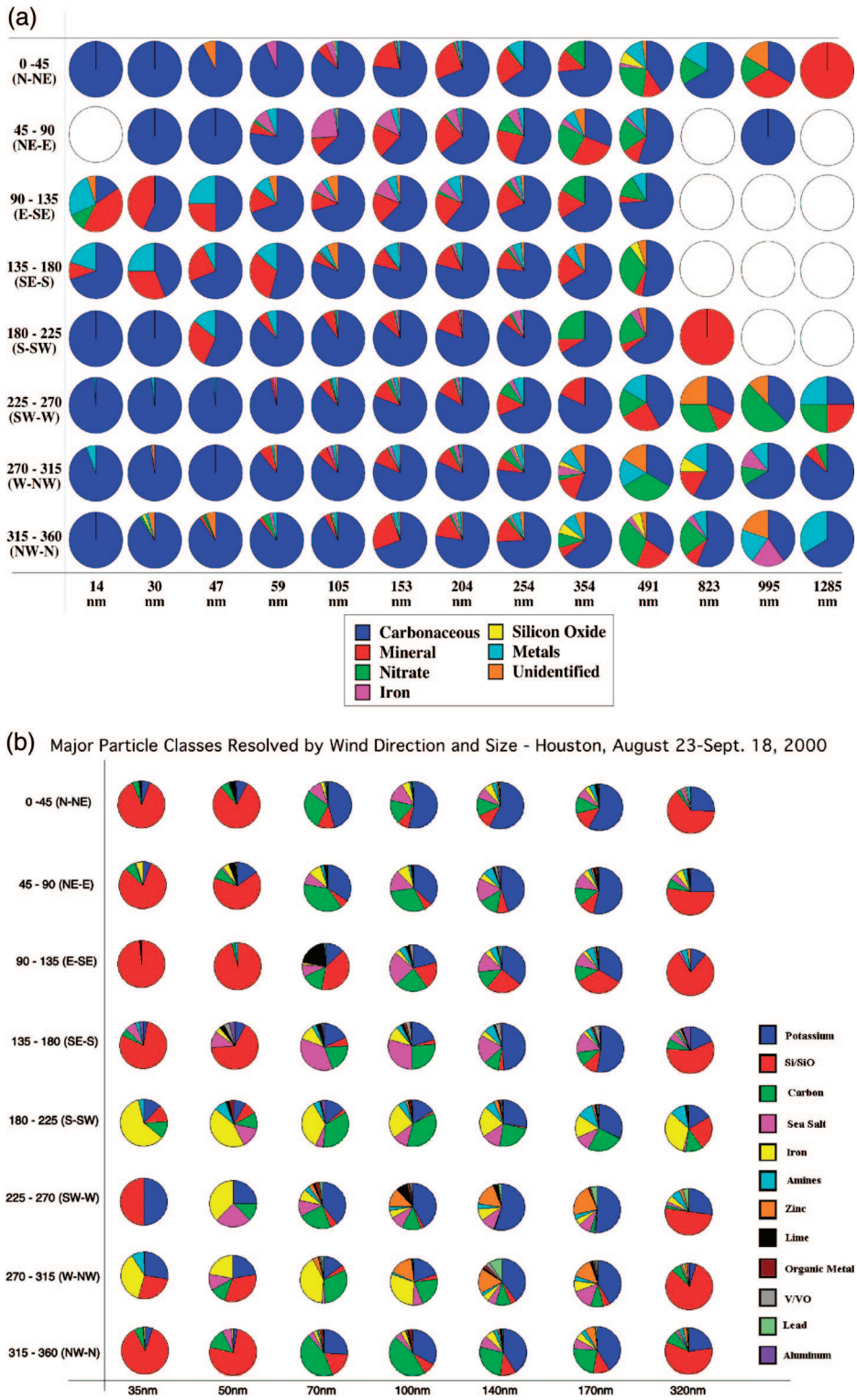


Figure 3. (a) Relative prevalence of the compound class groupings as a function of WD and particle size—Atlanta Supersites Project, August 1999. Particle mass spectra were classified into similar groupings on the basis of peaks present in the spectra and peak intensity. Each class represents a major grouping by chemical composition. For example, the carbonaceous class spectra contained peaks mostly related to carbon compound fragments. Figure 5 in Rhoads et al.[269] provides a sample mass spectrum for OC. Figures 6–14 in Rhoads et al.[269] provide example mass spectra for other species (K, Fe, Pb, Sn/Sb, Ca, nitrate, EC, and sodium [Na]/K). Reproduced/modified with permission from Rhoads et al.[269] Copyright 2003 American Geophysical Union, *Journal of Geophysical Research*. (b) Size- and wind-resolved particle class distributions, as detected by the instrument—Houston, TX, August 23 to September 18, 2000. Example mass spectra identifying the particle classes for K, silicon/silicon oxide, carbon, sea salt, Fe, Zn, amine (types 1, 2, 3), lime, V/vanadium oxide, organic mineral, Pb/K, Al, and lead salt are given in Phares et al.[268] Reproduced/modified with permission from Phares et al.[268] Copyright 2003 American Geophysical Union, *Journal of Geophysical Research*.

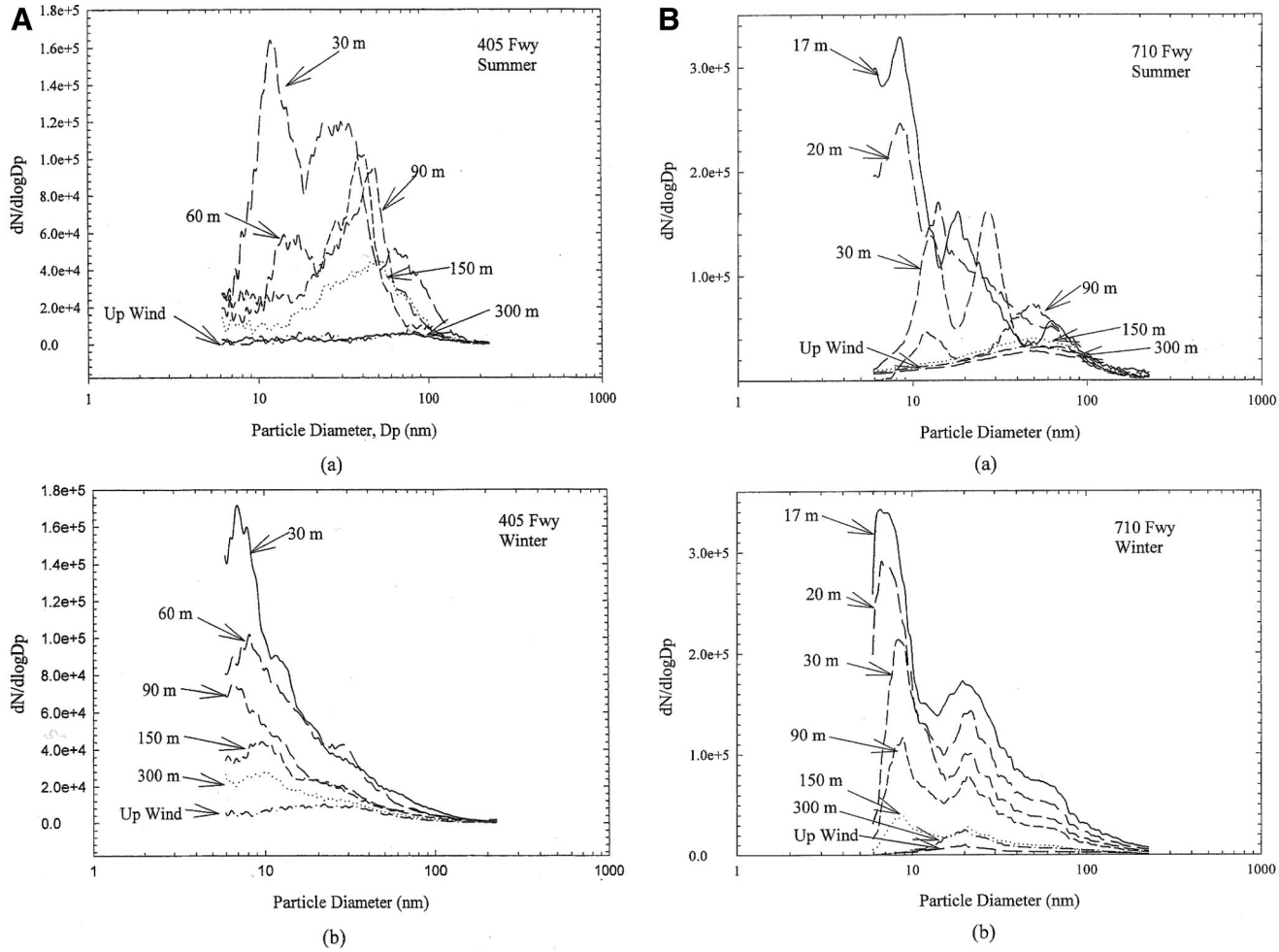


Figure 4. (A) UF PM particle size distributions at different sampling locations near the 405 freeway in (a) summer and (b) winter. Primarily light-duty gasoline vehicles use the 405 freeway. Reprinted with permission from Zhu et al.[275] Copyright 2004 American Asssociation for Aerosol Research, *Aerosol Science & Technology*. (B) UF PM size distributions at different sampling locations near the 710 freeway in (a) summer and (b) winter. During the study period, approximately 25–30% of the traffic on the 710 freeway was heavy-duty diesel vehicles. Reprinted with permission from Zhu et al.[275] Copyright 2004 American Asssociation for Aerosol Research, *Aerosol Science & Technology*.

appear to be formed following direct emissions from motor vehicles during morning rush hour. Increases in these smallest size-range particles also occurred often during the afternoon rush hour, most often in winter when the mixing heights remain lower than in summer. Strong afternoon nucleation events (>30,000/cm^3), peaking at around 1:00 p.m., were more likely to occur in spring and summer months. During these prominent nucleation events, peaks of SO_2 were strongly associated with the number concentrations of UF PM, whereas there were no significant correlations between these events and $PM_{2.5}$ and CO. Increased SO_2 concentrations were observed when the WD was from the northwest where three large SO_2 sources were located. It was hypothesized that UF PM formed during these events are H_2SO_4 and water from the oxidation of SO_2. There also were a more limited number of nucleation events followed by particle growth up to approximately 0.1 μm over periods of up to 18 hr. These nucleation and growth events tended to be common in spring months, especially in April. The local SO_2-related particle formation events occurred most frequently in August. In these events, SO_2 and UV-B rays were highly correlated, suggesting a high association of photochemical processing. These events also were highly correlated with northerly winds indicating the influence of the relatively local large-scale SO_2 point sources located in northwestern Rochester.

Results from the Supersites Program clearly indicate the lack of correlation between UF PM number and UF PM mass concentrations, UF PM mass (<100-nm particles) and $PM_{2.5}$ mass, and number concentrations (3- to 560-nm size range) and $PM_{2.5}$ mass.[99,103,166,178,214,275,277–280,282] UF PM, although high in number, comprise only a small portion of $PM_{2.5}$ mass (e.g., 5% in Pittsburgh[177]). These results are important because well-established methods exist to measure UF PM number concentration and size distribution (e.g., SMPS) and $PM_{2.5}$ mass, but not UF PM mass, although a method has been recently developed.[99] Thus, $PM_{2.5}$ mass cannot act as a surrogate for UF PM particle number concentration or UF PM mass, which is important if adverse health effects are associated with UF PM mass because only $PM_{2.5}$ mass and its chemical components are measured in routine national monitoring networks. A study in Los Angeles also looked at particle number concentration and

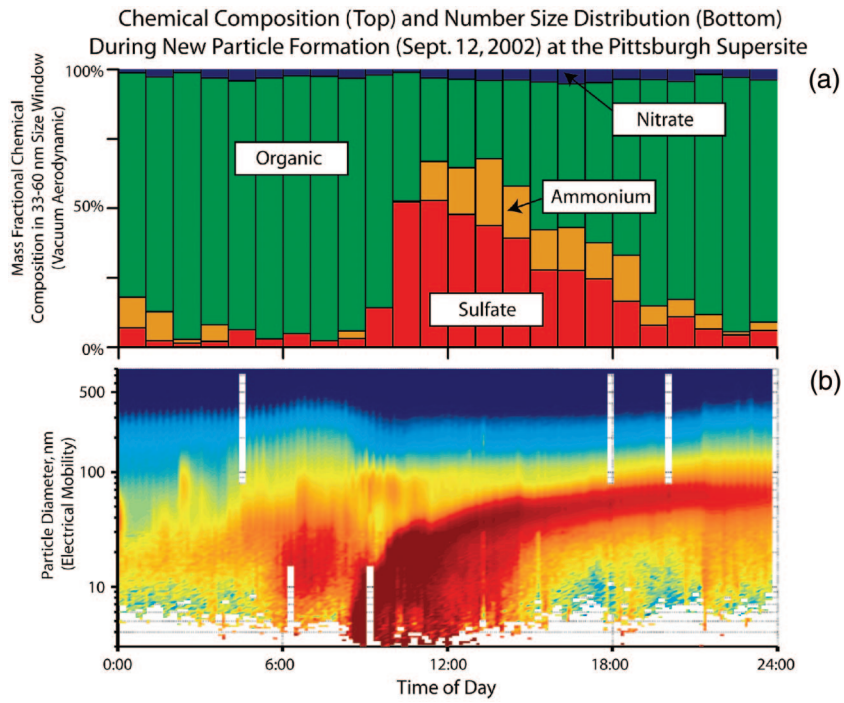


Figure 5. Diurnal behavior of UF PM (a) chemical composition and (b) number size distribution are illustrated on a day with intense new particle formation (September 12, 2002). Before 9:00 a.m., the UF PM particles are mainly organic and have a mode at 20–30 nm, consistent with primary emissions from combustion sources. At around 9:00 a.m., new particle formation is evident at sizes below 10 nm. This is followed by growth of the new particles and a rapid increase in the fraction of sulfate (initially) and $(NH_4)_2SO_4$ (later) in the UF PM particles. Aerosol chemistry is measured by an AMS for particles with vacuum aerodynamic sizes from 33 to 60 nm, or approximately 18- to 33-nm physical diameters. More information on September 12, 2002 and other events are given by Zhang et al.[290] Figure courtesy of C. Stanier, Carnegie Mellon University, Pittsburgh, PA (now at University of Iowa, Iowa City, IA) in association with the Pittsburgh Supersites Project and Q.I. Zhang, University of Colorado, Boulder, CO. Reproduced/modified with permission of Zhang et al.[115] Copyright 2005 American Geophysical Union, *Journal of Geophysical Research*.

gaseous pollutants (CO, NO, NO_2, and O_3) and observed weak to moderate correlations between particle number and gas phase pollutants, indicating that these pollutants can not be used as a surrogate to assess human exposure to UF PM.[292]

With the completion of the Supersites Projects' field programs, the only known continuing long-term measurements of particle size distributions and likely even particle number concentrations within the United States is occurring in Rochester, NY. Therefore, it is suggested that additional long-term studies (e.g., routine monitoring by state and RPOs, and nationally by EPA and EPA-funded studies begin to include these and related variables so that an adequate assessment of the health effects from UF PM can be obtained. The methods to make these measurements (e.g., CPC, SMPS) are commercially available, evaluated, and widely used in short-term research studies.

Aerosol Water and $PM_{2.5}$ Mass Balance

The hygroscopic behavior or amount of water associated with PM was measured using a tandem differential mobility analyzer (TDMA) during the summer and early fall of 2001 at three sites in Houston.[293] Measurements were in eight discrete particle sizes in the range from 25 to 700 nm. Hygroscopicity increased with increasing particle size, which suggested that condensation of less hygroscopic primary organic compounds onto the smallest particles measured (25 nm) was responsible for initial growth, noting that little is known about the initial particles smaller than 25 nm. Further growth likely was achieved by condensation of H_2SO_4 and other inorganic species as well as oxidized organic compounds.

A new method developed during the Pittsburgh Supersites Project provided continuous estimates of PBW for aerosols throughout the entire size range from 3 nm to 10 μm.[117] Examination of measurements from July 2001 to June 2002 indicated that water was an important constituent of $PM_{2.5}$ aerosol mass in the summertime (on average ~16% of the $PM_{2.5}$ FRM mass; equilibrated and weighed at 35% RH) and only a minor component in the winter.[90,119] In the summer, water accounted for most of the underestimation of the sum of the species relative to the FRM mass.[90] The higher water content in the summer was likely due to the higher levels of water-soluble species ($(NH_4)_2SO_4$, NH_4HSO_4, and SVOC) versus higher levels of primary OC in the winter, similar to results observed in Houston.[293] Results for 1 week in July showed an aerosol water content ranging from 0 to 50% or 0 to 20 $\mu g/m^3$ of water at RH values below 90%, with $PM_{2.5}$ mass concentrations ranging from around 5–60 $\mu g/m^3$, indicating that water can vary significantly during short time periods.[117]

Rees et al.[90] used continuous composition data and PBW (DAASS) measurements relative to mass measured by the SES-TEOM and was able to close the mass balance for aerosols collected in July 2001 at the Pittsburgh Supersite on an hourly basis. Khlystov et al.[119] and Rees et al.[90] also

showed that the maximum water retention occurred when the aerosol was acidic, with a significant portion of the sulfate as NH_4HSO_4.[115] This was further confirmed by Coz et al.[529] based on correlation of particle morphology with aerosol acidity. In the winter, when the aerosol is composed of higher fractions of primary OC and NH_4NO_3, along with $(NH_4)_2SO_4$, little water is associated with the aerosol. Khlystov et al.[119] also showed that water was retained on the aerosol in Pittsburgh at RH down to 30% in the summer, but was essentially dry below 60% in the winter. These results suggest that lower RH conditioning (likely below 30%) will be required to fully remove the PBW from acidic $PM_{2.5}$ samples. The role of aerosol acidity and SOA was discussed earlier in the SOA section.

More recently, Grover et al.[294] used a suite of continuous methods to obtain an approximate mass balance on an hourly time scale. Samples were collected in Rubidoux, CA, during July and August of 2005. They measured both semi-volatile and nonvolatile components (e.g., SVOC and OC using a dual-channel Sunset carbon analyzer) and major ions using an IC-based continuous method. The sum of the major components (carbon, sulfur, and nitrogen) were compared with the FDMS-TEOM, which measured total mass after PBW was removed; thus, PBW was not required to close the mass balance as was done in Pittsburgh.[90] Under the conditions studied, excellent agreement was obtained with a zero-intercept, slope close to 1, and $r^2 = 0.86$.

Measurements Aloft

Vertical distributions of aerosols were obtained using LIDAR during the 1999 Atlanta Supersites Project[5] and during the Baltimore Supersites Project.[295] Adam et al.[295] obtained measurements in Baltimore, MD, when the city was impacted by long-range transport of smoke from wildfires north of Quebec, Canada. The aerosol extinction coefficient indicated multiple aerosol layers in the vertical direction during smoke impact periods. The estimated index of refraction for the study period was $1.5 \pm 0.47i$, indicative of soot. The aerosol extinction coefficient was estimated and ranged from 0.01 to 1.05 1/km. A radar profiler also was used in Atlanta to measure wind speed and direction as well as related variables in the vertical direction[5] that are useful for understanding transport in the Atlanta region. These were the only aloft measurements conducted directly at Supersites Projects.

Aloft measurements were conducted at related study locations and included in SIRD. During the July 2001 ESP intensive monitoring period, LIDAR measurements were conducted in Philadelphia, PA, as part of the Northeast Oxidant and Particle Study (NE-OPS).[296] Aerosols in the lower troposphere were measured at night using a multistatic arrangement consisting of three imaging devices and a monostatic LIDAR during NE-OPS. The presence of strong, altitude-dependent layers was observed within the planetary boundary layer during much of the study. Three aircraft were coordinated during each of the ESP intensive monitoring periods. Flight paths for these aircraft are illustrated in Figure 6. Two aircraft operated out of the Lake Michigan area funded by Lake Michigan Air Directors Consortium (LADCO) and one operated out of the Washington, DC, area as part of the Maryland Aerosol

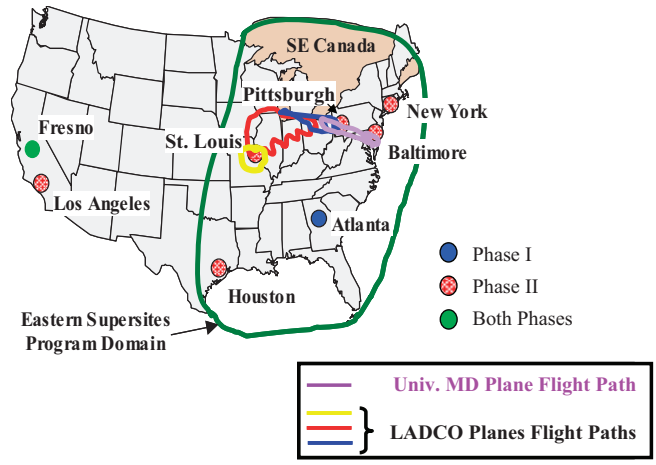


Figure 6. Generalized flight paths conducted by LADCO and Mid-Atlantic study aircraft during the ESP intensive monitoring periods in July 2001, January 2002, and July 2002.

Research and Characterization (MARCH-Atlantic) study[536] and the Regional Atmospheric Measurement, Modeling, and Prediction Program (RAMMPP).[297] The LADCO flights focused on the Ohio River Valley, St. Louis, and the Lake Michigan area, providing data to better understand pollution episodes in these areas, particularly transport from the upper Ohio River Valley back to St. Louis and Lake Michigan. LADCO flights also included Pittsburgh to link the LADCO data to the Maryland aircraft data. The Maryland aircraft primarily flew in the Maryland-to-Pittsburgh corridor to better quantify pollution transport from the west to the Mid-Atlantic states. Gas and aerosol measurements, the latter including physical properties, and $PM_{2.5}$ mass and composition (depending on the plane) were obtained aboard these aircraft. Observations and results relating to the Canadian wildfires based on the Maryland aircraft and LIDAR measurements were discussed earlier. Both LIDAR and aircraft measurements reaffirmed that multiple vertical layers exist within and above the boundary layer, as observed previously in California's San Joaquin Valley (SJV) and along the East Coast, as well as the importance of transport aloft with potential downmixing later in the day or the next day (Solomon et al.[298] and references within). Radar profiler measurements of wind speed and direction and related variables in the vertical obtained by the National Oceanic and Atmospheric Administration (NOAA) nationally and by the Mineral Management Services (MMS) on the Gulf Coast and by Rutgers University along the mid-Atlantic (Turpin, B., New Brunswick, NJ)[548] also are included in SIRD.

ESTIMATING SOURCE CONTRIBUTIONS AT RECEPTOR LOCATIONS

Two general approaches are used to estimate source contributions quantitatively at a receptor location(s): receptor-oriented methods and source-oriented methods. Receptor-oriented approaches are observationally based and apply statistical or similar approaches to ambient concentration data that are measured at a receptor site(s) to estimate source contributions at the receptor site(s). Information about the source may or may not be directly required depending on the approach applied. Source-

Table 9a. Important component marker species for major $PM_{2.5}$ sources.

Source	Descriptions	Marker Species
NH_4NO_3	Secondary aerosol	NO_3^-, NH_4^+
$(NH_4)_2SO_4$	Secondary aerosol	SO_4^{2-}, NH_4^+
SOA	Secondary aerosol	OC
Mobile	On-road gasoline and diesel vehicles; off-road mobile	OC, EC, EC1[a], EC2[a], NH_3, S, Fe, Zn
Cooking	Indoor and outdoor cooking	OC, EC
Fires	Wild forest fires	OC, EC, K^+, Cl^-
Waste burning and disposal	Agriculture burning, incineration, prescribed burning	OC, EC, K^+, As, Pb, Zn
Industrial fuel combustion	Electric utility, cogeneration, oil and gas production; petroleum refining; manufacturing and industrial; food and agriculture processing; service and commercial	SO_4^{2-}, Se, V, Ni, OC, EC
Residential fuel combustion	Wood combustion, cooking and space heating	OC, EC, K^+, Cl^-
Industrial processing	Chemical, food and agriculture, mineral processes, metal processes, wood and paper, glass and related products, electronics	Zn, Pb, Cu, Mn, As, Hg
Farming operations	Tilling, harvesting, and growing; livestock	OC, NH_3, NH_4^+
Road dust	Paved and unpaved road dust by traffic	Al, Si, K, Ca, Fe
Fugitive windblown dust	Farm lands, pasture lands, unpaved roads	Al, Si, K, Ca, Fe
Construction and demolition	Building, road construction dust	Al, Si, K, Ca, Fe
Sea salt	Marine aerosol	Na^+, Cl^-

Notes: [a]EC1 and EC2 are the EC fractions evolved at 740 and 840 $\dot{C}$ in a 98% helium/2% oxygen atmosphere, following IMPROVE_A protocol.[547] NO_3^- = nitrate, NH_4^+ = ammonium, SO_4^{2-} = sulfate, S = sulfur, Cl^- = chloride, Hg = mercury. Reprinted/modified with permission from Watson et al.[303] Copyright 2008 Air & Waste Management Association, *Journal of the Air & Waste Management Association.*

oriented approaches start from the source of the emissions and use models or modeling systems (e.g., a chemical transport model [CTM]) to describe the transport, transformation, and fate of those emissions from the source to the receptor. Both receptor-oriented and source-oriented approaches have limitations because they are based on incomplete conceptual models. (See Vickery[165] for descriptions of conceptual models for nine regions of North America). It also is important to note that CTMs can be used to predict changes in PM mass and components observed at a receptor as a result of future or predicted changes in emissions (e.g., emissions reductions recommended through a SIP). Receptor models do not have this capability because they are observationally based. Source-oriented models also effectively link source and receptor for secondary PM air pollutants (e.g., sulfate, nitrate, SOA) but are not as effective as receptor models for tracking primary species; thus, there is a synergy between source- and receptor-oriented models, with application of both providing the most accurate picture of the impact of source emissions at receptor locations. Receptor models will be discussed first followed by a review of source-oriented approaches.

Receptor-Oriented Approaches

Receptor-oriented approaches may involve simple analyses, such as time-series analysis or correlation between or among pollutants, or more complex multivariate approaches, usually referred to as receptor modeling.[299–303] This section focuses on the latter, receptor models, and descriptions of other receptor approaches can be found in Seinfeld and Pandis,[301] Brook et al.,[302] and Watson et al.[303] and references within these publications.

Although receptor models can separate primary from secondary components, they are used most effectively to link primary species observed at a receptor to source types or categories (source apportionment) or individual sources (e.g., a specific emitter) (source attribution) and to quantify (value with an uncertainty estimate) the source contribution at the receptor. Secondary components are usually grouped by compound (e.g., $(NH_4)_2SO_4$, NH_4NO_3), but quantitative separation into source categories is usually not obtained. Source markers or tracers (i.e., usually multiple markers used to identify a given source type) are used to identify primary sources and these may include inorganic and/or organic species. Typical potential source markers are given in Table 9, a and b.

Fifteen receptor models were applied to data from the Supersites Program. Table 10 lists the models used at each location and associated references, whereas the table footnote defines the acronyms for each model. Different models require different inputs. Inputs include ambient concentrations, at a minimum, with the option of one or more of the following: source profiles (fractional contribution of a species in a given source); meteorological variables such as WD or back trajectories; or (for the most recent model, the Pseudodeterministic Receptor Model [PDRM]) meteorological parameters required for Gaussian plume dispersion estimates, stack engineering parameters (height, exit velocity, etc.), and high-time resolution chemical data.[157,304] PDRM is a hybrid model because it uses aspects of both typical receptor modeling and Gaussian plume dispersion modeling. In all cases, results depend on the model used, the input data (e.g., number of species measured in the ambient sample and supplemental data), and the experience of the investigator.

The three most widely used models are CMB,[305–307] positive matrix factorization (PMF),[308] and UNMIX.[309] All three are based on the general mass balance equation and require ambient concentration measurements.[303] PMF and UNMIX require only ambient concentrations, and the factors developed are interpreted by the investigator as specific source types (e.g., motor vehicle, soil dust, etc.). Specific source information is not required for PMF and

Table 9b. Potential organic marker species for major $PM_{2.5}$ sources.[64,303]

Organic Aerosol Sources	Specific Organic Markers	Important Organic Markers/Source Indicators
Gasoline-powered engine exhaust		Hopanes, steranes, PAHs, EC
Diesel engine exhaust		Hopanes, steranes, EC
Natural gas combustion		PAHs
Fuel oil combustion		Hopanes, steranes, EC, Ni, V
Coal combustion—uncontrolled	Picene	Hopanes, steranes, PAHs, EC
Biomass burning (cellulose) (associated sources: wildfires, forest fires, residential wood combustion—Fine et al.)[444,445,478]	Levoglucosan	Resin acids, methoxyphenols, phytosterol, β-sitosterol, stigmasterol, campesterol, saccharides
Soft wood burning (associated sources: wildfires, forest fires, residential wood combustion—Fine et al.)[444,445,478]	Resin acids	
Hard wood burning (associated sources: wildfires, forest fires, residential wood combustion—Fine et al.)[444,445,478]	Syringyl derivatives	
Fugitive dust from cultivated land (associated sources: wildfires, forest fires)	Saccharides: mycose, sucrose, α-, β-glucose	
Meat cooking	Cholesterol	Tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, palmitin stearin
Plastic waste burning		Even carbon alkanes
Vegetative detritus		*n*-Nonacosane, *n*-triacontane, *n*-hentriacontane, *n*-dotriacontane, *n*-tritriacontane
Leaf surface waxes (associated sources: burning vegetative detritus, soil dust, vegetarian cooking)		Odd-carbon *n*-alkanes ($>C_{25}$); Even carbon *n*-alkanoic acids ($>C_{23}$)
Cigarette smoke	iso-Nonacosane, anteiso-triacontane, iso-hentriacontane, anteiso-dotriacontane, iso-tritriacontane	
SOA	1,2-Benzenedicarboxylic acid, methyl-1,2-benzenedicarboxylic acid	Not well defined

UNMIX, although previously measured source profiles may assist in the interpretation of the profiles calculated by the models. CMB requires the assumption that the sources are known and that source profiles are available for each source. EPA has supported the development of these three models for use in the regulatory process, and their use is becoming integral to the development of SIPs. Current information about these models can be found at http://www.epa.gov/scram001/receptorindex.htm. Current EPA version numbers are CMB8.2 (http://www.epa.gov/scram001/receptor_cmb.htm), PMF 3 (http://www.epa.gov/heasd/products/pmf/pmf.htm), and UNMIX 6 (http://www.epa.gov/heasd/products/unmix/unmix.htm).

Other factor analysis models with ambient concentrations as the primary input include PMF-Multilinear Engine (PMF-ME), Partial Least Squares (PLS), and Non-Negative Least Squares (NNLS). These models typically allow for source types to be identified, but not necessarily a specific emitter. Inclusion of meteorological parameters allows for source location, and thus, identification of specific emitters.[310] Several of these models are applicable to identifying the location of local sources using surface WD in the analysis and include Conditional Probability Function (CPF) and Non-Parametric Regression (NPR), whereas others are applicable to regional sources using back trajectories in their analysis. These latter models include Potential Source Contribution Function (PSCF), Residence Time Analysis (RTA), Trajectory Sector Analysis (TSA), Simplified Quantitative Trajectory Bias Analysis (SQTBA), and Residence Time Weighted Concentrations (RTWC) (see Table 10 for relevant references for each model). Each model has certain strengths and weaknesses and often the use of two or more with a given dataset allows convergence on the best solution.

PDRM likely represents the largest step forward in receptor modeling and, in fact, begins to form a bridge (hybrid model) between receptor modeling and source modeling, because PDRM uses a Gaussian plume model within its framework.[157,304] The Gaussian plume model is used to constrain solutions to the mass balance model. PDRM uses the dispersion information from the Gaussian model along with high-time resolution ambient data, knowledge of the number and locations of major stationary sources, source transport WDs and distances, and stack gas emissions parameters to predict the contributions to ambient concentrations from known stationary sources and emissions rates of specific pollutants from the individual sources. The model using 30-min average SEAS trace element data[153,154] and other supporting data has been successfully applied in Tampa, FL, and Pittsburgh, PA.[157,304] An example of the observed and predicted results for a series of trace elements along with specific source identification is provided in Figure 7.

Table 10 lists 44 applications of various receptor models to Supersites Program data, including major and minor components, organic species data, and the high-time resolution elemental data collected with the SEAS in Tampa, FL. Ambient concentration datasets applied in these models

Table 10. Sources identified by receptor modeling approaches in programs associated with EPA's PM Supersites Program and related studies.

Location	References	Models Applied (see footnote for definition of acronyms)[a]	Factors or Sources Resolved in Study, Listed in Order of Highest to Least Important Factor when Provided	Comments
Atlanta, GA	Kim et al.[310]	PMF, ME with WS and WD	SO_4^{2-}-rich secondary aerosol I Gasoline exhaust Diesel exhaust NO_3^--rich secondary aerosol Metal processing Wood smoke Airborne soil SO_4^{2-}-rich secondary aerosol II Cement kiln with a carbon-rich source	August 1998 and August 2000; 24-hr particle composition monitor samples (Atmospheric Research, and Analysis, Inc.); species included SO_4^{2-}, NO_3^-, NH_4^+, OC, EC, trace elements by XRF, surface WS and WD; the expanded model (ME) aided in separating diesel exhaust from gasoline vehicle exhaust, and two sources of SO_4^{2-}
	Kim et al.[479]	PMF, CPF	$PM_{2.5}$ Secondary aerosol SO_4^{2-} and NH_4^+ Motor vehicle Wood smoke Secondary aerosol NO_3^- and NH_4^+ Cement kiln and OC Airborne soil Metal recycling facility Bus station and metal processing PM_c Airborne soil Secondary aerosol NO_3^- Secondary aerosol SO_4^{2-} Cement kiln Metal recycling facility (1%)	August 1998 and August 2000; 24-hr particle composition monitor samples (Atmospheric Research, and Analysis, Inc.); $PM_{2.5}$ (26 variables) and PM_c (15 variables) including mass, major ions, and trace elements in both size ranges; EC/OC was only measured in $PM_{2.5}$; SO_4^{2-} was higher in the summer; PMF with CPF more clearly identified point sources, e.g., including WD in the analysis for both $PM_{2.5}$ and PM_c clearly showed the direction of the cement kiln; a metal recycling source and bus station also were identified
	Kim et al.[480]	PMF	Secondary SO_4^{2-} I On-road diesel Secondary NO_3^- Wood smoke Gasoline vehicle Secondary SO_4^{2-} II Metal processing Airborne soil Railroad traffic Cement kiln/carbon-rich Bus maintenance facility/ highway traffic	August 1998–August 2000; 24-hr particle composition monitor samples (Atmospheric Research and Analysis, Inc.); species included SO_4^{2-}, NO_3^-, NH_4^+, OC, EC (plus OC and EC fractions by TOR/ IMPROVE analysis method), trace elements by XRF, surface WS and WD
	Liu et al.[481]	PMF	Secondary SO_4^{2-} Wood smoke Secondary NO_3^- Diesel exhaust Gasoline exhaust Industrial factor I Crustal material Coal combustion Industry factor-II	January 2000–December 2002; Jefferson St.; 24-hr speciated PM data including OC and EC fractions by TOR; CO, SO_2, HNO_3, and NO_y; OC/EC ratio in gasoline and diesel factors are 2.07–2.36 and 0.82–0.98, respectively
Southeastern and eastern United States	Zheng et al.[60]	CMB	Secondary SO_4^{2-} Wood combustion Diesel exhaust Secondary NH_4^+ Secondary NO_3^- Meat cooking Gasoline-powered motor vehicle exhaust Road dust 2 (2%)	April, July, and October 1999 and January 2000; four urban and four rural/suburban sites in Alabama, Florida, Georgia, and Mississippi (SEARCH sites); 24-hr samples; OC species and major components, OC species samples were composited monthly; wood combustion was higher during the colder months and higher percentages of unexplained fine OC was observed in July, likely because of an increase in SOA; results compared to CMAQ source apportionment (Bhave et al.[375])

Table 10. (cont.)

Location	References	Models Applied (see footnote for definition of acronyms)[a]	Factors or Sources Resolved in Study, Listed in Order of Highest to Least Important Factor when Provided	Comments
Southeastern and eastern United States (cont.)	Zheng et al.[234]	CMB/carbon isotope analysis	Wood combustion Gasoline exhaust Diesel exhaust Meat cooking Vegetative detritus Cigarette smoke Road dust Natural gas Coke facilities Unexplained (SOA or other primary sources	September 2003 and January 2004, at three urban (Alabama, Florida, Georgia) and one rural site (Alabama paired with urban site); OC species and via high-volume sampling, inorganic species by standard filter-based methods and analysis; fossil sources: diesel exhaust, gasoline exhaust, natural gas combustion, and coke production; contemporary carbon: wood combustion, meat cooking, vegetative detritus, cigarette smoke, and road dust; CMB and ^{14}C agreed
Pittsburgh, PA	Pekney et al.[314,315]	UNMIX, PMF, CPF, PSCF	PMF and UNMIX Secondary SO_4^{2-} NO_3^- Crustal material Fe/Mn/Zn OC/EC Specialty steel Cd PMF additional Ga Pb Se PSCF and CPF SO_4^{2-} Crustal material Vehicle emissions and road dust Wood combustion Ga-rich Steel production Pb Specialty steel Cd Se	July 2001–July 2002; 24-hr data and single-particle data; filter data included standard chemical components and several OC species; specialty steel was likely the coke production plant; PMF with organic markers split the primary OC/EC factor in two—vehicles and wood smoke; CPF and PSCF analysis on NO_3^-, mobile, wood smoke, and cooking factors lead to inconclusive results regarding local vs. regional sources, identified as both; PSCF and CPF applied to PMF apportioned data
	Cabada et al.[482]	OC/EC tracer method, mass balance box model	SOA OC (annual average basis) Wood burning (highest in winter) Fugitive combustion sources Steel industries Mobile sources EC (annual average basis) Heavy- and light-duty diesel trucks Coke-burning steel related industries Stationary fuel combustion sources Fugitive sources	1995; emissions inventory developed and SOA was calculated based on OC/EC tracer method; and sources quantified using a mass balance box model; SOA—ranged from <10% in the winter to 50% in the summer, annual average 35%; local wood burning was highest in the winter; results were compared to ambient data, greater seasonal variability was observed in the ambient data than the modeled results
	Pekney et al.[316]	PMF, single-particle classes and WD	Local specialty steel Steel mill SE of site Internally mixed Pb northwest unknown source Coal combustion northwest of site Lack of oil combustion	July 2001–July 2002; Apportioned trace element data only (Pekney and Davidson[42]); ICP-MS from high-volume samples and single-particle data; composition and size distribution of particle classification provides source signature; results confirm previous work (Pekney et al.[314,315])
	Zhou et al.[317]	PMF, CPF	Sparse nucleation Local traffic Stationary combustion Grown particles and remote traffic Secondary aerosol	July 2001–July 2002; particle size distribution data 3 nm to 2.5 μm; inferred sources in order of decreasing number concentration; size-distributions were correlated with gas and particle data and estimated WD by CPF

Table 10. (cont.)

Location	References	Models Applied (see footnote for definition of acronyms)[a]	Factors or Sources Resolved in Study, Listed in Order of Highest to Least Important Factor when Provided	Comments
Pittsburgh, PA (cont.)	Zhou et al.[323]	ME, CPF, NPR	Secondary SO_4^{2-} Secondary NO_3^- Traffic Crustal material Steel mill Coke plant	Mid-July 2001 (5 days); multiple time-resolution measurements including semicontinuous $PM_{2.5}$ ions (1 hr), elements (10 min), and OC/EC (2–4 hr), and NO, NO_x, CO, SO_2, and ozone (10 min); sources not fully separated because of small dataset
	Zhou et al.[319]	PMF, CPF	Secondary and aged primary aerosol Stationary combustion sources Remote Pittsburgh traffic Local traffic (15 nm) Local nucleation (<10 nm)	July 2001–June 2002; 15-min average size distribution data (3 nm to 1.8 μm); apportioned size distribution data; factor 1 and 2 accounted for ~91% of particle volume; chemical composition data used for relating factors but not in source apportionment
	Zhou et al.[318]	PMF, PLS, NPR	Secondary NO_3^- I (0.80 μm) Secondary NO_3^- II (10 nm)[#] Remote traffic Secondary SO_4^{2-} Pb Diesel traffic Coal-fired power plant Steel mill Nucleation Local traffic Coke plant	July 16–24, 2001; size distribution, aerosol composition (species collected with 30 min averages or less), only used 30-min average or less PM (SO_4^{2-}, NO_3^-, elements) and gas (ozone, NO_x, SO_2, CO) data; PLS collaborated relationship between size distributions and composition allowing PMF as a tool for apportionment [#]Related to local traffic
	Park et al.[304]	PDRM	Four coal-fired boilers	April 1, 2002 (6:00 a.m. to 6:00 p.m.); SO_2 and 30-min average elements collected by SEAS; determined emissions and ambient source contributions rates of SO_2 and elements from four coal-fired boilers influencing the Carnegie Mellon University (CMU) Supersite location; SO_2 and trace elements agree to within ~5% of observed emissions rates; source profiles obtained by PDRM and are all within the range of previous in-stack measurements
	Shivastava et al.,[483] Subramanian et al.[484]	CMB, PMF of OC and $PM_{2.5}$	OC SOA Food cooking Motor vehicle Biomass burning Vegetative debris Metallurgical coke production Other primary $PM_{2.5}$ (25% of days with OC species) SO_4^{2-} PBW NH_4^+ SOA Other primary Cooking Coke production Wood smoke	July 2001–July 2002, 100 days; 24-hr average $PM_{2.5}$, EC, elements, OC species, and on fewer days, SO_4^{2-} and NO_3^-; primary OC contributed ~25 and 50% of the total OC in summer and winter, respectively, approximately two-thirds of the primary OC is transported into Pittsburgh; sampling artifacts and photochemical degradation of markers had little impact on the apportionment results; of the 25 days examined for $PM_{2.5}$, two-thirds occurred in the summer and in the summer inorganic ions account for up to 50% or more of the $PM_{2.5}$ mass and SOA is a significant fraction of the remaining $PM_{2.5}$ mass

Table 10. (cont.)

Location	References	Models Applied (see footnote for definition of acronyms)[a]	Factors or Sources Resolved in Study, Listed in Order of Highest to Least Important Factor when Provided	Comments
Pittsburgh, PA (cont.)	Bein et al.[485]	Gaussian plume dispersion modeling	Three coal-fired power plants	October 27, 2001 (6:00 a.m. to 2:00 p.m.), single-particle MS (RSMS III), particle class consisting of Na/Si/K/Ca/Fe/Ga/Pb composed 60% of the particles detected; class associated with three power plants; total particle number emissions rates were estimated ranging from 6×10^{15} to 1.4×10^{17} particles/sec; cars at freeway speeds emit $\sim 3 \times 10^{12}$; estimates to $PM_{2.5}$ NEI were within 20–30% for two plants and 50% of the NEI for the other; SO_2 and NO_x emissions rates also were obtained
	Eatough et al.,[324] Modey et al.[217]	PMF, UNMIX, and observed back trajectories	Secondary sources Secondary transport (mostly $(NH_4)_2SO_4$) from west and southwest Midday photochemistry Major local source of SOA (photochemical) Primary sources Mobile diesel Mobile gasoline Minor sources Crustal Incinerator Industrial emissions Coal-fired power plant	July 2001 intensive; NETL site southwest of Pittsburgh Supersite; data included $PM_{2.5}$ mass data from four per day, 24-hr PC-BOSS filters, TEOM, NO_x, NO_2, ozone, non-volatile, semi-volatile, and volatile OM, EC, SO_4^{2-}, and PIXE determined trace metals; transport of both primary and secondary material from sources along the Ohio River Valley[486] (ORV) and 85% of the long-distance-transported $PM_{2.5}$ was secondary $(NH_4)_2SO_4$
	Martello et al.[531]	PMF2, PSCF and HYSPLIT calculated back trajectories	Secondary transported (dominated by $(NH_4)_2SO_4$) Secondary local Mobile diesel Mobile gasoline Crustal material Coal-fired power plants Steel mill Wood smoke High Zn, Fe High As High Pb, Fe	October 1999–September 2001; NETL site southwest of Pittsburgh Supersite; $PM_{2.5}$ FRM mass, semi-volatile $PM_{2.5}$ OM, EC, trace elements; secondary SO_4^{2-} dominated transported material (sources from ORV important contributor), local primary and secondary account for 45% of PM mass split 43% local primary, 57% local secondary; results similar to July 2001 intensive study[217,324]
	Millet et al.[187]	Factor analysis	Winter Local automotive[#] Natural gas[#] Industrial emissions Primary and secondary components (VOC and PM) Secondary mixed Coal Summer Local automotive[#] VOC (secondary + biogenic)[#] Transport Industrial[##] Isoprene oxidation products Natural gas[#]	January–February and July–August 2002; semicontinuous VOC ($\sim$50 species), trace gases; SO_4^{2-}, NO_3^-, number concentrations (3–10 nm, 100–500 nm ranges); apportioned VOC and aerosol species data in Pittsburgh [#]No PM contribution to factor; [##]PM weakly loaded, but not significant; SOA = 16% winter, 37% summer; local motor vehicle primary factor driving changes in VOC levels; they did not contribute significantly to aerosol species in Pittsburgh

Table 10. (cont.)

Location	References	Models Applied (see footnote for definition of acronyms)[a]	Factors or Sources Resolved in Study, Listed in Order of Highest to Least Important Factor when Provided	Comments
Pittsburgh, PA (cont.)	Robinson et al.,[206,207,209,235] Subramanian et al.[208]	Ratio-ratio plots complimenting CMB analysis	OC sources Motor vehicle (gasoline and diesel) Biomass smoke Food cooking emissions Metallurgical coke production Photochemical aging	July 200–July 2002; organic marker species, EC, other major components as complimentary data; photochemical aging and choice of marker species increases uncertainty of CMB results as well as multiple and varying source profiles from the same source type; variations in food cooking were a factor of 9
Fresno, CA	Chen et al.[487]	UNMIX, PMF	Secondary NO_3^- Residential wood combustion Motor vehicle Zn Dust Vegetative detritus Sea salt Farming	January 2000–January 2001; 24-hr averaged $PM_{2.5}$ mass, elements, ions, OC, EC, and thermal carbon fractions; Zn factor is thought to have mobile origin
	Schauer and Cass[62]	CMB	Urban Wood combustion Diesel exhaust Gasoline exhaust Meat cooking Gas combustion Rural Wood combustion Diesel Road dust Vegetative detritus	December 1995–January 1996; 24-hr average OC, Fresno, Bakersfield, Kern Wildlife Refuge; ~75 organic aerosol species, VOC species; apportioned OC only using organic aerosol and VOC species, with supplemental chemical aerosol data; 84% of OC mass not extracted; SO_4^{2-}, NO_3^-, and SOA account for most of $PM_{2.5}$ mass; wood combustion most important source in urban areas; IMS95 study (Solomon and Magliano[488])
	Chow et al.[38]	CMB	Secondary NO_3^- Cooking Vegetative burning Gasoline vehicle Secondary SO_4^{2-} Dust Diesel Sea salt	December, 1999–January, 2001; 24-hr averaged $PM_{2.5}$ with organic markers (semi-volatile PAH, hopanes and steranes, and polar compounds); annual average results for Fresno; dust higher in summer at all sites; vegetative burning (residential wood smoke) higher in winter at all sites
Houston, TX	Zhao et al.[223]	CMB-ME	Species identified as individual factors and related to sources by WD Acrylonitrile Isoprene and vinyl acetate C7-ketone Toluene and xylene Benzene Styrene Acetic acid C9- and C10-benzenes Propane	August 2000–September 2000; LaPorte Municipal Airport; CMB of VOC species with parallel measurements and equation to account for WS, WD, temperature, and weekend/weekday effects; species determined with proton transfer reaction mass spectrometer Order not related to importance
	Fraser et al.[363]	CMB	Diesel vehicles Gasoline vehicles Road dust	August 29, 2000–September 1, 2000 (1 hr at noon, 2 hr at 4:00 p.m.); tunnel study to evaluate separation of diesel and gasoline vehicles by CMB using PM mass, OC, EC, and semi-volatile PAHs, hopanes and steranes, and polar compounds; obtained emission indexes using CO and CO_2 measurements

Table 10. (cont.)

Location	References	Models Applied (see footnote for definition of acronyms)[a]	Factors or Sources Resolved in Study, Listed in Order of Highest to Least Important Factor when Provided	Comments
Houston, TX (cont.)	Fraser et al.[394]	CMB	Diesel vehicles Gasoline-powered vehicles Paved road dust Oil combustion Meat cooking Vegetative detritus Wood combustion	March, 1997–February, 1998; three urban and one background site; 24-hr averaged $PM_{2.5}$ mass, elements, ions, OC, EC, thermal carbon fractions, semi-volatile PAH, hopanes and steranes, and polar compounds; urban sites higher than background for all source contributions, oil combustion only observed at ship channel site; seasonal differences noted for some contributions, but not all
	Dechapanya et al. [390]	FAC, primary tracer using EC	Point sources contribute most to SOA (53%) (pulp and paper processing most important) [aromatics (especially toluene, xylenes, and trimethylbenzenes) and anthropogenic terpene] Mobile (9%) Area, non-road (38%)	January–December 2000; determined fraction of SOA formed from organic species from emissions inventory using FAC approach; emissions inventory indicates area and non-road mobile sources contribute 56%, mobile sources contribute 27%, and point sources contribute 16% of OC mass; SOA results indicate point sources (53%), non-road (37%), mobile (10%); comparison to GPPM indicates relative agreement, but FAC may be high by factor of 2
	Russell and Allen[179]	EC/OC tracer method	Primary OC SOA	August 15, 2000 to August 15, 2002; 24-hr average OC and EC; primary carbon greater than SOA at all sites, SOA highest in September with maximum ozone, primary OC highest November/January–February, primary OC highest at urban sites
	Lemire et al.[212]	Primary tracer using $^{13}C/^{14}C$ ratio	Modern (biogenic) carbon Fossil carbon	August 2000; $^{13}C/^{14}C$; biogenic (modern) SOA account for up to 80% of SOA north of Houston (forested areas) to as little as not detectable in urban Houston (similar to Vizuete et al.,[241] Yue and Fraser[63]); EC and MC correlated so EC influenced by forest fires, cooking, and vegetative detritus in southeast Texas
	Buzca and Fraser[489]	PMF	All three sites Petrochemical production Refinery Natural gas Gasoline (evaporative) Aromatics Industry Walisville additional Biogenic sources Vehicle exhaust/transient industrial	June–October 2003; 54 VOC species (1-hr average) by automated GC; three sites located in Houston Ship Channel
New York, NY	Dutkiewicz et al.[39]	TSA	Regional SO_4^{2-} Local SO_4^{2-}	July 2001 to June 2002; 24-hr averaged $PM_{2.5}$ mass, SO_4^{2-}; Queens (urban) and two rural (Whiteface Mt., Pinnacle State Park); apportionment by trajectory analysis; 44–55% of SO_4^{2-} transported on an annual basis to Queens, ~60% to rural sites; highest SO_4^{2-} occurs when air comes from ORV and Great Lakes Basin, moderately high from Mid-Atlantic states

Table 10. (cont.)

Location	References	Models Applied (see footnote for definition of acronyms)[a]	Factors or Sources Resolved in Study, Listed in Order of Highest to Least Important Factor when Provided	Comments
New York (cont.)	Dutkiewicz et al.[192]	TSA, PT (Se)	Regional Se (91% transported from coal combustion to the west, As, Pb, V, Sb) Secondary SO_4^{2-} Sb (source to the north) Local Oil combustion (no. 6 heating oil) (Ni, Co, <50% of V, Sb, Zn) V (likely local sources)	July, 2001 to September 30, 2002; 24-hr PM SO_4^{2-} and 15 metals by ICP-MS; Queens (urban site)
	Li et al.[490]	PMF	Secondary SO_4^{2-} Road dust Sea salt Secondary NO_3^- Oil combustion Motor vehicle	July 2001; 6-hr averaged $PM_{2.5}$ mass, elements, ions, and OC (by AMS); PILS-IC (SO_4^{2-}, NO_3^-, Na, K); good agreement for NO_3^- and SO_4^{2-} between AMS, PILS, and filters
	Liu et al.,[426] Zhou et al.[322]	PMF, PSCF, SQTBA, RTWC	Secondary SO_4^{2-} Soil Secondary NO_3^- Wood smoke Ni smelter Cu smelter Zn smelter	May 15, 2000 to August 31, 2000; Potsdam and Stockton, NY; 24-hr $PM_{2.5}$ mass, ions, BC, elements, and 20 PAHs; all but Ni smelter are seen in Stockton, and the relative contributions are slightly different between Stockton and Potsdam; SO_4^{2-} factor contains almost no PAHs, whereas wood smoke contains the highest PAH content; PSCF shows a common source region of SO_4^{2-} extending from the lower Great Lakes to south of the ORV
	Bari et al.[491]	TSA	Transported vs. local (within 150 km) $PM_{2.5}$ mass Secondary SO_4^{2-} Precursor gases	January 1999–November 2000; NYC, two sites; HNO_2, HNO_3, HCl, SO_2, NH_3, SO_4^{2-}, $PM_{2.5}$ mass; annual average basis ~40% SO_4^{2-} from Midwest (60% from within 150 km), 30% $PM_{2.5}$ mass and about 15–25% of the PM precursor gases were transported with remaining amounts due to local sources
St. Louis, MO	Lee et al.[327]	PMF, CPF	Secondary SO_4^{2-} Carbon-rich sulfate Gasoline exhaust Secondary NO_3^- Steel processing Soil Diesel Zn smelting Pb smelting Cu production African dust	June 1, 2001 to May 31, 2003; 24-hr averaged $PM_{2.5}$ mass, ions (including NH_4^+), elements, OC, EC, and thermal carbon fractions (TOR/IMPROVE protocol); secondary SO_4^{2-} and NO_3^- accounted for ~65% of the $PM_{2.5}$ mass; likely source region for SO_4^{2-} is ORV; Saharan dust event observed in July 2002 Summertime pollution episodes in St. Louis and upper Midwest often occur on the back side of high-pressure system as the system moves from west to east across the ORV and into the northeastern United States[537]

Table 10. (cont.)

Location	References	Models Applied (see footnote for definition of acronyms)[a]	Factors or Sources Resolved in Study, Listed in Order of Highest to Least Important Factor when Provided	Comments
St. Louis, MO (cont.)	Lee and Hopke[326]	PMF, PSCF, CPF	Blair Secondary SO_4^{2-} Secondary NO_3^- Motor vehicle Soil Cu smelting Zn smelting Steel processing Arnold Secondary SO_4^{2-} Gasoline exhaust Secondary NO_3^- Calcium Diesel Soil Pb smelting Metal processing Biomass burning	February, 2000 to December 2003; 24-hr $PM_{2.5}$ mass, elements, ions, OC, EC (NIOSH method) (a total of 26 species used for Blair site and 23 species used for Arnold site); both urban sites; PSCF identified SO_4^{2-} and NO_3^- as regional sources; higher secondary SO_4^{2-} in summer with the ORV as a likely source region; NO_3^- is influenced by NH_3 sources in Iowa and Kansas; African dust can contribute about 3% to the PM mass, regional sources (51–60%), mobile sources (17–26%), local industrial plants (21%)
	Brown et al.[385]	PMF, CMB	Mobile sources, including on-road and non-road, gasoline and diesel, and smoking (high-emitting) and nonsmoking vehicles Burning (both residential wood combustion and wildfires) Industrial sources SOA	February 2004 to February 2005; St. Louis Supersites and upper Midwest; five STN urban and one IMPROVE rural sites, major components by networks plus OC speciation; local sources are more important than transport; OM is higher at urban than rural sites and higher in summer, suggesting SOA in addition to primary OC
	Kim et al.[325]	PMF, PSCF	Summer high secondary SO_4^{2-} Secondary NO_3^- Gasoline vehicle OP-high, secondary SO_4^{2-} Se-high, secondary SO_4^{2-} Airborne soil Aged sea salt Diesel emissions	March 2001 and May 2003; Bondville, IL; IMPROVE data with carbon fractions; highly elevated airborne soil impacts may be due to Asian and Saharan dust storms OP-pyrolyzed OC
	Zhao et al.[332]	SQTBA, RTWC	SO_4^{2-} NO_3^-	2000–2003; sites in the midwestern United States, including two rural sites and urban sites in Chicago, Cleveland, Detroit, Indianapolis, and St. Louis; only NO_3^- and SO_4^{2-} were used in the analysis; SO_4^{2-} from long-range transport from the ORV, NO_3^- locally generated influenced by high NH_3 concentrations.
Baltimore, MD	Ogulei et al.[492]	PLS, PMF, CPF	Wildfire (Canadian fire) Secondary SO_4^{2-} Secondary NO_3^- II Coal-fired power plant Local gasoline traffic Incinerator Secondary NO_3^- I Soil/road dust Oil-fired power plant Diesel Steel plant Nucleation	August 2002 (6 days); particle size distribution (9 nm to 2.5 μm), $PM_{2.5}$ mass, ions, elements, mass, CO, NO_x, and ozone; 97.7% of the measured $PM_{2.5}$ mass explained with size-distribution and composition data; two NO_3^- factors may be due to nucleation (smaller size) and transport; UF PM associated with diesel and gasoline vehicle but not wildfire emissions

Table 10. (cont.)

Location	References	Models Applied (see footnote for definition of acronyms)[a]	Factors or Sources Resolved in Study, Listed in Order of Highest to Least Important Factor when Provided	Comments
Baltimore, MD (cont.)	Ogulei et al.[493]	PMF-ME, CPF	Spark-ignition emissions Secondary SO_4^{2-} Secondary NO_3^- Steel plant Incinerator Coal-fired power plant Oil-fired power plant Diesel emissions Aged sea salt	Mid-November 2002; focus on using variable time resolution; 30-min average SO_4^{2-}, NO_3^-, 11 elements, 1-hr average OC and EC, and 24-hr average ions, OC, EC, and elements; most SO_4^{2-} and NO_3^- regional; SO_4^{2-} associated with coal-fired power plants in heavily industrialized midwestern United States.; steel plant (<10 m, 141° southeast) also significant; regional sources contribute > 45% of $PM_{2.5}$ mass
Tampa, FL	Park et al.[157]	PDRM	SO_2 and selected trace element emission rate estimates for four utility plants Four oil- and coal-fired power plants and two industrial sources (Cargill Fertilizer and Gulf Coast Pb-battery-recycling plant) all located within a 70° arc from 200°–270° and distance from >10 to 41 km from the site	May 13, 2002; 30-min average SO_2, metals (30-min time resolution) using SEAS; excellent agreement for SO_2 to within ~8% of observed emissions rates; source profiles obtained by PDRM are all within the range of previous in-stack measurements
	Pancras et al.[156]	Time-series analysis, PCM, PMF	Source profiles for specific sources not previously reported Animal feed supplements production facility Incinerator plume (included burning of pressure treated lumber) Other sources identified Battery recycling plant including two coal-fired blast furnaces Two power plants Soil dust	May 2002 (Sydney, FL), November 2002 (Dairy, FL); 11 trace elements by SEAS (30-min average), SO_2, NO_x, 24-hr $PM_{2.5}$; 10 sampling days based on certain WDs Time-series analysis with WD allowed for identification of specific sources and source plumes impacts from which source profiles were obtained; PCM and PMF allowed for separation of overlapping sources

Notes: [a]CMB = chemical mass balance, PMF = positive matrix factorization, ME = multilinear engine (not a stand-alone model, but a solver that allows multiple variables), UNMIX = refers to unmixing the sources, PDRM = pseudo-deterministic receptor model, PLS = partial least squares, PT = primary tracer, NNLS = non-negative least squares, FAC = fractional aerosol coefficient, CPF = conditional probability function, NPR = nonparametric regression, TSA = trajectory sector analysis, PSCF = potential source contribution function, SQTBA = simplified quantitative transport bias analysis, RTWC = residence time-weighted concentrations, WD = wind direction, WS = wind speed.

ranged from less 1 day (e.g., Tampa, FL) to datasets that extended over 3 yr. Most often datasets ranged from several days to a year. Results provided in Table 10 have been generalized to include only the sources identified in each analysis and not the quantitative contribution, although the often-inferred factors or sources are typically listed in order from highest to lowest contributor as reported in the cited papers. In general, for similar datasets the results are reasonably consistent for major contributors, although differences in the specific order are observed. Larger differences are observed for minor contributors, often where the source may be identified with one model, but not another, in part, because of the use of different species in the dataset as mentioned below.

As seen in Table 10, many chemical components of PM are measured for use in receptor-modeling approaches. These include inorganic species, such as trace metals, organic species or classes of organic species (e.g., functional groups[73]), and more recently, physical property data such as size distributions, as mentioned below. Several organic species have been identified as potential marker species (e.g., see Table 9b).[62,69,78,80,311,312] Use of these markers for source apportionment has allowed for continued application and advancement in receptor modeling over the last 10–15 yr,[60,62,80] especially as distinctive inorganic tracers have been removed from sources (e.g., Pb from gasoline).

The ideal particle marker or tracer species would be emitted by only one source category and be stable in the atmosphere. This latter assumption has recently been questioned for several organic tracer species[207,235,313] on the basis of lifetimes of $PM_{2.5}$ observed in the eastern United States where regional emissions tend to dominate (estimated aerosol residence times of 1–3 weeks[218]). Robinson et al.[207,235] and Subramanian et al.[208] used ratio-ratio plots to isolate photochemical aging of several important tracer species. Ratio-ratio plots are constructed with data for three species—two target compounds whose concentrations are normalized by the same reference compound. This method is

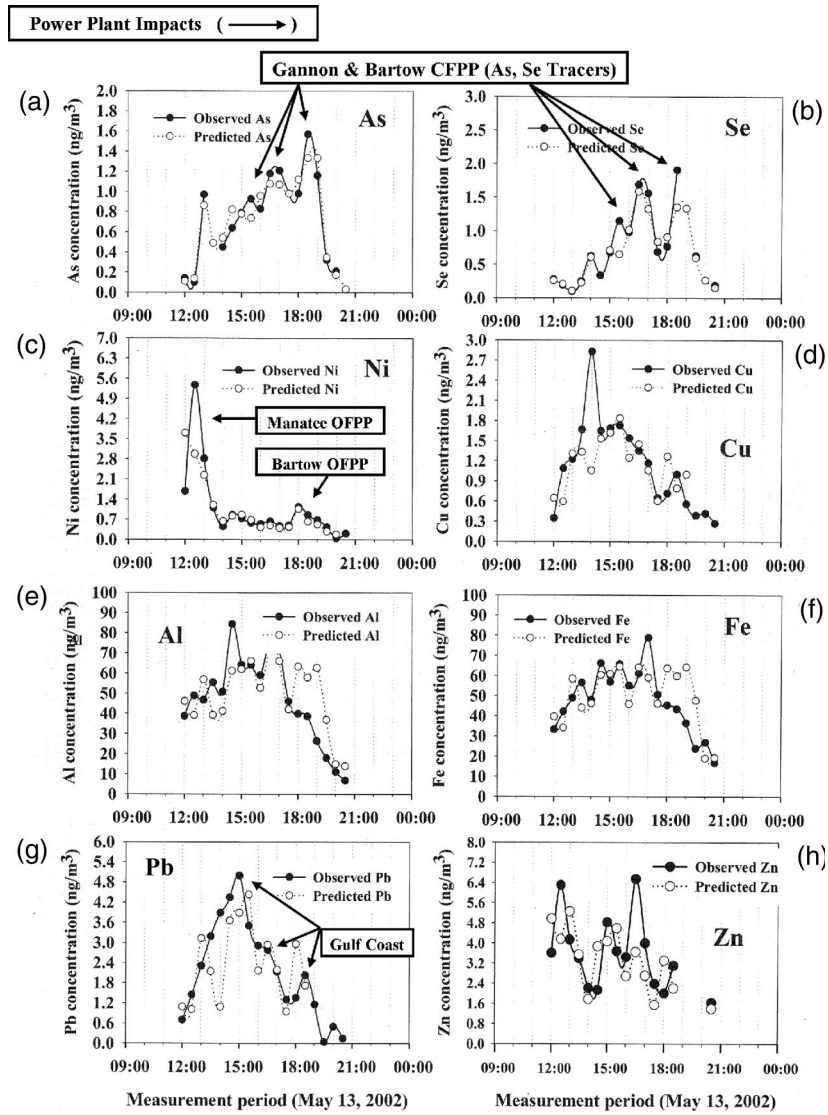


Figure 7. Observed and PDRM-predicted concentrations of elemental species are illustrated for data collected at the BRACE study site, Tampa, FL, May 13, 2002 for (a) As, (b) Se, (c) Ni, (d) Cu, (e) Al, (f) Fe, (g) Pb, and (h) Zn. Noted are examples of sources identified because of estimates based on WD and Gaussian plume dispersion estimates. Gannon is a coal-fired power plant (As and Se as tracers), Manatee and Bartow have coal- and oil-fired boilers, and Gulf Coast is a Pb-battery recycling plant and burns coke and natural gas. Reproduced/modified with permission from Park et al.[157] Copyright 2005 American Geophysical Union, *Journal of Geophysical Research*.

illustrated using synthetic data in Figure 8A, panel a. Ambient data fall along or between lines of mixing when emitted by two or more sources (i.e., mixing of emissions from multiple sources), whereas source profile data appear as points. Using the extensive organic species dataset from the Pittsburgh Supersites Project, Robinson et al.[206,207,235] and Subramanian et al.[208] indicate that some species, such as specific PAHs (markers for various combustion sources), hopanes (motor vehicle markers), and alkenoic acids (cooking markers) undergo significant and nonlinear degradation by photochemical oxidation within regional air masses (e.g., residence times of days to weeks). This is in contrast to laboratory chamber studies in which the species are allowed to react for much shorter periods of time.[65] However, the oxidation rate of oleic acid and other alkenoic acids in real atmospheric particles is slower than in laboratory experiments conducted with single-component particles.[207]

Ratio-ratio plots also provide insight into potential source profile combinations for use in CMB modeling as well as allowing for an examination of uncertainties in the measurement of marker species in various source profiles.[206–209,235] The method is intended to compliment quantitative source apportionment methods such as CBM or PMF. Figure 8, B–E, illustrates the application of ratio-ratio plots through four examples. A simple case is illustrated in Figure 8B, in which emissions from one large source, metallurgical coke production, dominates PAH concentrations. Hopanes, markers for motor vehicle emissions, provide a more complicated case. Ambient ratios of hopanes vary by season, include a mix of emissions from several sources types (gasoline and diesel vehicles), and undergo photochemical aging as shown in Figure 8C. The

result is a seasonally varying gasoline-diesel split.[208] Figure 8D shows a situation with an unknown source profile because the ambient data cannot be explained by mixing lines defined by any combination of known source profiles. Here, the choice of any of the existing source profiles would result in significant uncertainty in the CMB solution. The last example (Figure 8E) illustrates how multiple source profiles can be used to fit markers for meat cooking resulting in a more confident CMB solution. Figure 3 in Robinson et al.[209] illustrates the case for biomass smoke, the most complicated example. Ambient ratios for biomass smoke vary widely because of the large number and varied types of source profiles (sources).

Apportionment results also are highly dependent on the model inputs (ambient data) and the model applied. For example, secondary species such as sulfate and nitrate will not be apportioned if only trace elements are used as input data. Conversely, if only sulfate, nitrate, OC, EC, and a few organic compounds are used, many industrial sources, crustal material, and sea salt may not be identified. To illustrate this further, several groups performed analyses using data from the Pittsburgh Supersites Project covering the period from July 2001 to July 2002. Pekney et al.[314,315] applied several models (PMF, UNMIX, CPF, and PSCF) using a fairly complete chemical dataset that included major chemical components, trace elements, and several organic markers. Pekney et al.[316] apportioned only trace elements from high-volume sampling and ICP-MS analysis and single-particle data as well as WD using PMF. Zhou et al.[317] applied PMF and CPF to size distribution data (3 nm to 2.5 μm) collected in Pittsburgh during the July–August 2001 ESP intensive monitoring period. Zhou et al.[318] then followed up with a similar analysis using data collected in Pittsburgh during a full year beginning in July 2001 (the full ESP monitoring period). Later, Zhou et al.[319] applied PMF, PLS, and NPR to size distribution data, high-time resolution composition data (30-min averages or less), and gases. Pekney et al.[314] apportioned seven factors/sources using UNMIX and PMF, and an additional three factors were identified by PMF, yet they did not identify nucleation, gasoline vehicles, or diesel vehicles, or even a more general category referred to as traffic. Pekney et al.[315] identified 11 source types with general locations and distance from the receptor site (regional, local, both). Using only size distribution data, Zhou et al.[319] were able to separate out nucleation and traffic, but not several of the sources that Pekney et al.[314–316] were able to separate, such as specialty steel, sulfate, and nitrate (although Zhou et al.[318] had a secondary aerosol factor), nor several other minor sources. Pekney et al.[316] apportioned several specific source types that were not identified by the others as well, including coal combustion (at a given direction, northwest of the site), steel mill southeast of the site (different from specialty steel), and an internally mixed unknown Pb source northwest of the site. Finally, Zhou et al.[318] identified 11 sources using PMF, PLS, and NPR with an extensive input dataset including chemical composition and size distributions. PMF results are illustrated in Figure 9. The relationship between size distribution and chemical composition was collaborated with PLS, allowing PMF to be applied. Eleven factors are about twice the number of sources identified using standard 24-hr filter-based chemical composition data (sulfate, nitrate, ammonium, OC, EC, trace elements). These examples described above and others in Table 10 clearly illustrate the advantages to using high-time resolution chemical and physical attributes (e.g., size distribution data) and single-particle data in receptor modeling.

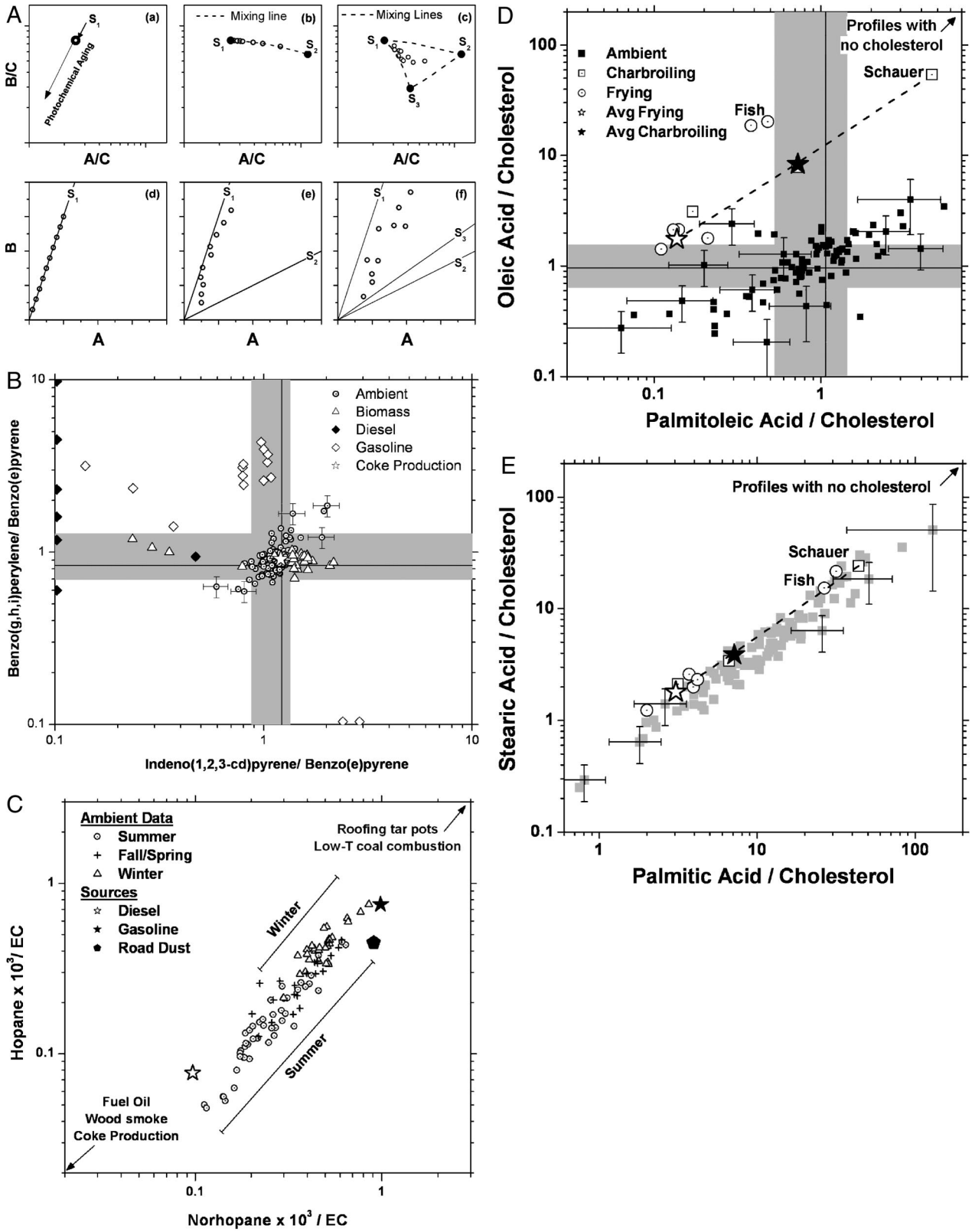
Lee and Russell[320] evaluated uncertainties in CMB apportionment results by examining uncertainties in both ambient measurements and source profile input data. Uncertainties in source profile data were larger and had a greater influence on CMB apportionment results than ambient measurement data. Thus, reducing source profile uncertainties can lower uncertainties in source apportionment results. Obtaining updated emissions profiles from major primary sources (some profiles were developed in the 1980s), as well as representative profiles (because in some cases only one profile existed for a particular source) will help to reduce source apportionment uncertainties.

Thus, results from the Pittsburgh Supersites Project and elsewhere indicated that the influence of nonlinear aging, choice of source profiles, uncertainty in source profiles, and choice of markers species can result in significantly different CMB solutions, albeit the solutions have high statistical quality.[206] This of course has important implications if only CMB were used for the development of SIPs.

Trajectory analysis showed consistent impacts of long-range transport of sources in the Ohio River Valley impacting, for example, New York (urban and rural sites),[39,192,220,321,322] Pittsburgh,[217,323,324] and St. Louis and the upper Midwest.[325–332] The latter may sound somewhat surprising with transport from the east to St. Louis; however, this occurs because of transport of pollutants along the backside of a high-pressure system moving from west to east.[537] Chu et al.[163] also noted this phenomenon based on CTMs of STN sites. Trajectory analysis also helped confirm the impact of the July 2002 Canadian fires and the regional nature of the fires across the northeastern United States.[162] For St. Louis[326] and other sites in the upper Midwest,[328–331] trajectory analysis of particulate nitrate suggested the importance of NH_3 source areas rather than showing strong relationships with the likely NO_x source regions.

Single-particle data have not been widely used to apportion sources by receptor modeling,[333] but other approaches in which the particles are separated into classes of similar size and/or composition and internally mixed or externally mixed particles has been achieved. One example is the Adaptive Resonance Theory version 2a (ART-2a),[334] which was applied to data collected by the RSMS III.[219,270,271,335] Results indicated that externally mixed particles usually fall in the lower size range (<100 nm) and are associated with fresh local emissions, whereas internally mixed particles are usually associated with larger particle sizes (>100 nm) and result from condensation or coagulation of other species onto existing particles (e.g., Tolocka et al.,[219] Zhang et al.,[115] Bein et al.,[335] and Zhao et al.[223]). Such work provides a wealth of information on the atmospheric processes that give rise to the observed individual particles.

The AMS provides size-resolved measurements of individual nonrefractory components of $PM_{2.5}$ in high-time resolution.[115] Sources categories were identified by statistical analysis and temporal and spatial variations in the size distributions and chemical composition. For example, Zhang et al.[115] estimated contributions from primary and secondary aerosols and combustion versus those formed through photochemistry. For the latter, morning aerosols consisted of organic components associated with primary combustion sources, whereas the afternoon organic aerosols were associated with oxygenated organic compounds. Zhang et al.[248,249] also classified AMS spectra



into HOA and OOA. HOA, as mentioned earlier, was related to diesel exhaust, lubricating oil, and freshly emitted traffic aerosols observed in urban areas, whereas OOA closely resembled aged oxidized organic aerosols typically observed in rural areas. Thus, results of single-particle spectrometers and AMS provide a wealth of information on sources on the basis of size-resolved chemical composition. These methods and approaches are just beginning to be implemented in apportioning source impacts at receptor locations. See *Methods, Development, and Evaluation* for additional information on AMS and single-particle mass spectrometers as well as reviews by Canagaratna et al.[114] and Sullivan and Prather.[158]

Source-Oriented Approaches

The Models. Source-oriented approaches start from the emissions source of the pollutant and work forward in time (rather than starting from the receptor and working backwards in time) to estimate the contribution of a source(s) at a receptor location(s). Source-oriented approaches use advanced mathematical models or modeling systems to describe the fate of those emissions between the source and the receptor (e.g., Russell,[336] Seigneur and Moran,[337] and references within these papers). The most advanced source-oriented modeling systems (referred to here as a CTM to follow the NARSTO convention, Seigneur and Moran[337]) integrate our knowledge about the fate of pollutants emitted into the atmosphere, are Eulerian-based, and consist of three major components: an emission model, meteorological model, and an atmospheric process model (here referred to as the chemistry model). Each model also may be composed of several modules.

The Supersites Program did not include specific objectives related to source-oriented modeling, although model performance and testing were implied as part of objective two, "to elucidate source-receptor relationships … on urban and regional scales." As a result, limited model performance and application were conducted by Supersites Programs and related studies and the focus, therefore, was on atmospheric process models/modules as described by Russell[336] and summarized in this section. To a lesser extent emissions models were evaluated by comparing emissions estimates with ambient data and these comparisons are described by Simon et al.[338] and briefly summarized in the emissions section (see *Emissions: Estimates, Inventories, and Uncertainties*).

Model Performance Evaluations. Seigneur et al.[339] indicated that an improved model performance evaluation for CTMs likely would be obtained if high-time resolution air quality data were available. This would allow those evaluating CTMs to move beyond operational evaluation ("Are we getting the right answer?") and to begin initial diagnostic, and if needed mechanistic, evaluations that give additional insights to ask the question "Are we getting the right answer for the right reason?" As with meteorological models, limited ambient data also are used to nudge or adjust the modeled concentrations to measurements during the model run, and thus, improve agreement between the models and remaining ambient data. Nudging is most effectively accomplished with high-time resolution data.

Because evaluation and application of source-oriented modeling requires the development of emissions inventories, meteorological fields, and large ambient datasets for comparison and perhaps for boundary and initial conditions, source-oriented modeling comes at the end of a measurement and modeling program, as is the case with the Supersites Program.[336] Thus, as yet, little information is available in the journal literature with regards to CTM performance evaluation and application for PM using Supersites Program data, although a few papers have been published, submitted, or are in preparation.[336,340–345] Furthermore, RPOs are funding modeling efforts, most using STN, IMPROVE, and Clean Air

Figure 8. (A) Scatter and ratio-ratio plots of simulated ambient data (indicated by open circles). The simulated data are based on mixing of emissions from up to three different sources: S1, S2, and S3. Plots a and d are one-source scenarios; plots b and e are two-source scenarios; and plots c and f are three-source scenarios. The arrow in plot a indicates how ambient ratios will change with photochemical aging, as discussed in the text in Robinson et al.,[235] Reprinted with permission from Robinson et al.[235] Copyright 2006 American Chemical Society, *Environmental Science & Technology*. (B) Ratio-ratio plot comparing ambient PAH to source profiles. The lines indicate the slopes of linear regressions shown in Figure 2a in Robinson et al.,[235] and the gray areas indicate 5th and 95th percentiles of the data. Source profiles are from Cadle et al.,[436] Watson et al.,[437] Schauer et al.,[311,438,439] Hays et al.,[440,441] Rogge et al.,[442,443] Fraser et al.,[393] and Fine et al.[82,444,445] Error bars are shown for a limited number of points to indicate the typical level of measurement uncertainty. Profiles plotted on the *y*-axis and/or *x*-axis do not report indeno(1,2,3-*cd*)pyrene and/or benzo(*g,h,i*) perylene emissions or have emission ratios outside the range of the plot. Reprinted with permission from Robinson et al.[235] Copyright 2006 American Chemical Society, *Environmental Science & Technology.* (C) Ratio-ratio plot of two hopanes normalized by EC for 96 daily samples collected in Pittsburgh, PA. Also shown are emission ratios for different sources of hopanes and EC. The gasoline and diesel profiles are averages of many published vehicle profiles.[311,393,441,442,437] The road dust profile is from Robinson et al.[370] Arrows point to sources that do not fall within the bounds of the plot, as discussed in Robinson et al.[207] With the exception of a few outliers, the winter data are tightly clustered near (0.5, 0.4). Fall/spring data are more spread out, extending to the lower left from the winter cluster along the 1:1 line. Summer data are even more spread along the same line. This is consistent with extensive oxidation during the summer, corresponding to a nondimensional lifetime (t/τ) between 0.5 and 1.5, relative to wintertime conditions. Reproduced/modified with permission of from Robinson et al.[207] Copyright 2006 American Geophysical Union, *Journal of Geophysical Research.* (D and E) Ratio-ratio plots comparing ambient data for the five cooking markers to source profiles.[312,446–448] The dashed line is a linear mixing line connecting the average frying and the Schauer et al.[312] charbroiling profile. The horizontal and vertical lines in (D) indicate the slopes of linear regressions of the oleic acid and the palmitoleic acid data vs. cholesterol (e.g., Figure 2b in Robinson et al.[206]). The gray areas in (D) indicate 20th and 80th percentiles of the data. The arrow in the upper right-hand corner of the plot points towards sources such as biomass combustion, motor vehicles, road dust, and seed oil cooking that emit the different acids but not cholesterol. Error bars are shown for a limited number of points to indicate the typical level of measurement uncertainty. The label "fish" indicates the two fish frying profiles, and the label "Schauer" indicates the Schauer et al.[312] charbroiling profile. Reprinted with permission from Robinson et al.[206] Copyright 2006 American Chemical Society, *Environmental Science & Technology*.

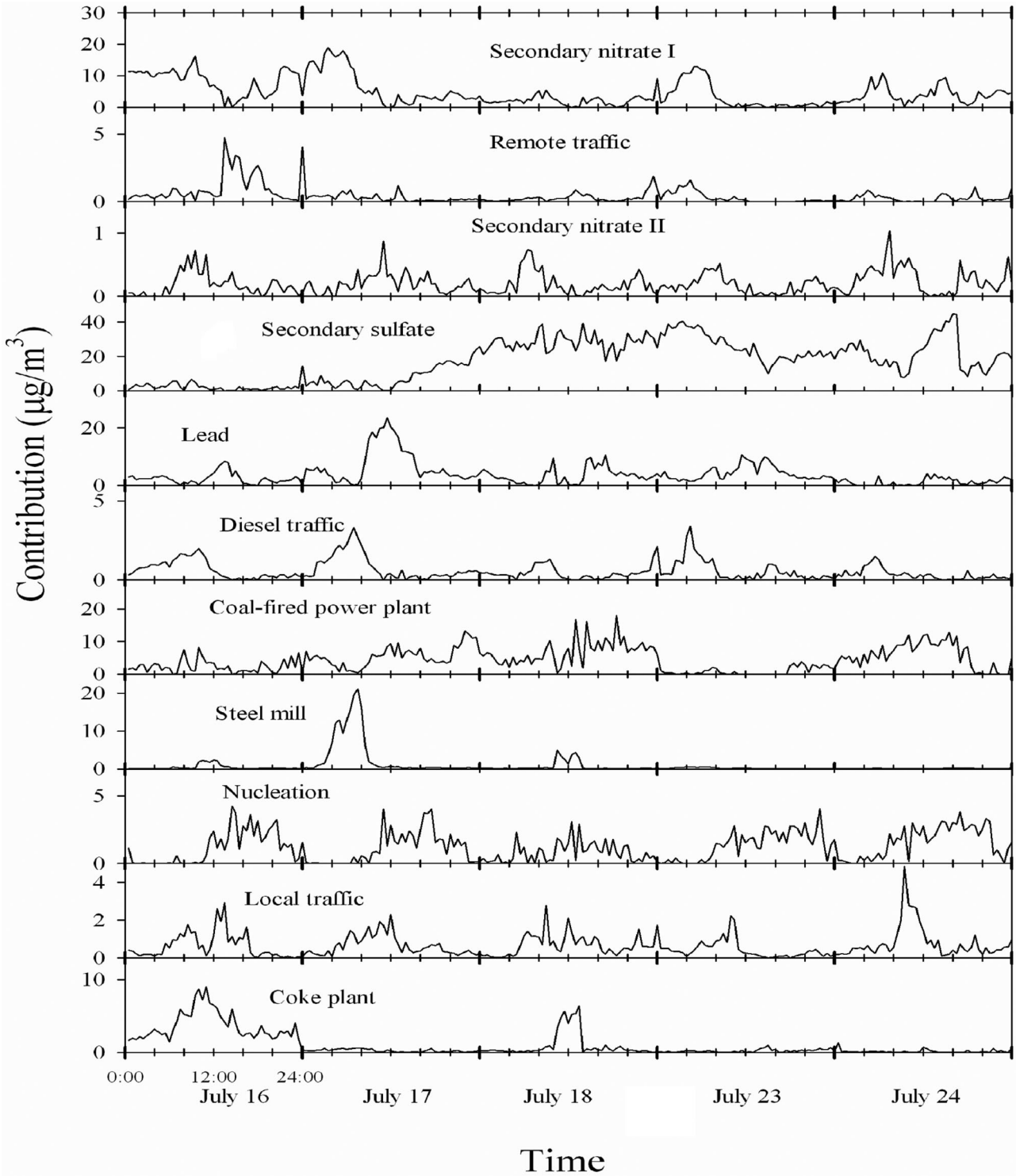


Figure 9. Source contributions from PMF analysis. Data were measured at the Pittsburgh Supersite July 16–18 and July 23–24, 2001. Reproduced/modified with permission from Zhou et al.[318] Copyright 2005 American Geophysical Union, *Journal of Geophysical Research*.

Status and Trends Network (CASTNet) data.[343,346,347] Boylan and Russell[343] have established goals and criteria for three-dimensional source-oriented model performance evaluation as described in more detail below.

Russell[336] summarizes the recent CTM (or module) performance studies that directly used either Supersites Program data or data from related studies; that is, data collected during the Supersites Program but not directly by a Supersites Project. SEARCH (other than the 1999 Atlanta Supersites Project) is an excellent example of a related study. Previous model performance evaluation studies are summarized in Seigneur and Moran.[337] Russell[336] breaks down model performance evaluation into three parts: (1) testing components, such as the thermodynamic equilibrium modules; (2) comparing models to measurements; and (3) model intercomparisons (CTM to

CTM and CTM to receptor model). Russell[336] also describes a model application and then extends the analysis to include a discussion of the relationship of PM to gaseous pollutants and precursor species, suggesting what changes in ambient PM concentrations might occur because of changes in precursor emissions.

Testing Components. Zhang et al.,[348] Takahama et al.,[349] Vayenas et al.,[350] and Yu et al.[344] evaluated the gas- to particle-phase distribution of the inorganic ionic species (sulfate, nitrate, and ammonium) using the thermodynamic equilibrium model (TEM) and Supersites Program data. These tests included evaluating a model that describes nucleation bursts in the eastern United States[278] that appear to be due to a ternary reaction system involving NH_3-H_2SO_4-water.[283,291] Results indicated that the TEMs predict the partitioning of sulfate (considered total sulfate), total nitrate, and total ammonium between the gas and aerosol phases reasonable well and often apparently within the error of the measurements. Reasons for initial and final differences between the simulations and observations or between the models included the following:

(1) The ambient environment may not be in equilibrium,[344,348] although it may be in equilibrium,[348] and the acidity (amount of sulfate in the system) may need to be adjusted slightly. For example, Zhang et al.,[348] found that a 15% adjustment to the observed sulfate brought the results into agreement for HNO_3 and NH_3.
(2) There may be problems with the TEMs.
(3) In the case where nitrate may not be partitioned satisfactorily (nitrate overestimated in the winter in Pittsburgh and underestimated in the summer in Atlanta[344,348,349]), there may be other mechanisms producing the observed nitrate.

Comparing Models to Measurements. Yu et al.[247] also compared results from the Community Multiscale Air Quality (CMAQ) modeling system to observations made during the same time periods used to evaluate the TEMs (August 1999 in Atlanta, January 2002 in Pittsburgh). They found that errors in sulfate production or total ammonium levels (e.g., biases in the emissions inventory for NH_3) account for much of the error in partitioning nitrate between the gas and aerosol phases. These authors also indicated that use of high-time resolution data allowed for a much better understanding of the causes of the differences between models (modules) and observations because everyday diurnal variations in the pollutants could be compared rather than just 24-hr averages that are typically available only once every 3 or 6 days. However, the 24-hr data have much greater spatial coverage.

Park et al.[341] used data from the 1999 Atlanta Supersites Project to evaluate the ability of CMAQ to simulate particle size distributions. Modeled number concentration was low by a factor of 2, especially at the smaller particle size ranges and that the differences were worse during days when nucleation events occurred. Apparently the physics of nucleation was not well described in the model and the model did not have a mode to capture the formation of the smallest particles. Morris et al.[346,347] performed CMAQ modeling in support of Visibility Improvement State and Tribal Association of the Southeast (VISTAS) (http://www.vistas-sesarm.org/), the RPO concerned with regional haze and NAAQS for PM in the southeastern United States. Morris et al.[346,347] initially used long-term data collected by STN and IMPROVE during ESP intensive measurement periods (August 1999, July 2001, and January 2002) and then high-time resolution data collected by SEARCH during the same times. Performance varied by species, with sulfate having the best performance (fractional bias values generally within 20%) and the other species varying by up to $\pm 100\%$, with the deviations often being different and opposite for summer and winter. Use of the hourly data greatly enhanced the understanding of these differences. Overall, to date, observed sulfate and ammonium concentrations in the southeastern United States were reproduced within reasonable uncertainties. The uncertainty or agreement for other species (EC, primary OC, SOA, nitrate, soil) was reproduced less well.

Park et al.[342] address an important uncertainty question regarding the comparison between models (a grid cell average) and ambient measurements (a point in space) using daily data collected in the southeastern United States during 2002, 2003, July 2001, and January 2002, the latter two periods representing ESP intensive monitoring periods. Their results indicate an error of up to 15% due to the inconsistency between making a point measurement versus a grid-cell average, noting grid cells may be 12×12 km^2 or 36×36 km^2 with surface level heights of tens to hundreds of meters. Thus, most of the observed difference between model simulations and observations was not necessarily because of point versus grid-cell comparisons.

Karydis et al.[351] evaluated Particulate Matter Comprehensive Air Quality Model with extensions (PMCAMx) against daily average $PM_{2.5}$ measurements collected by the IMPROVE and STN monitoring networks and the Supersites Program throughout the eastern United States during 2001–2002. The performance of the model in reproducing sulfate, organic mass, EC, and total $PM_{2.5}$ concentrations varied from average to good depending on the season. Uncertainties in NH_3 emissions during the fall caused errors in the corresponding ammonium predictions, whereas the NH_3 emissions inventory appeared to be satisfactory during other seasons. The ability of the model to reproduce aerosol nitrate concentrations in the spring and summer was limited by difficulties in simulating the heterogeneous nighttime formation rate of HNO_3. During the summer and fall, the model performance in reproducing the organic PM concentrations and diurnal patterns was good. During the summer, the predicted organic PM averaged 60% primary and 40% secondary. The secondary contribution to organic PM dropped to around 20% during the winter. The applied average EC emissions rate of approximately 0.55 kt/day (0.45 kt/day during the weekend) yielded estimates consistent with the observed EC concentrations.

Karydis et al.[351] and Gaydos et al.[352] took advantage of the Supersites Program's continuous $PM_{2.5}$ measurements to improve the model descriptions of HNO_3 dry deposition, nighttime mixing, heterogeneous chemistry,

etc. The same continuous measurements have been valuable in identifying the potential causes of model errors that are by no means obvious from comparisons of daily average measurements.

Model Intercomparisons. Morris et al.[346] reported on a comparison of CMAQ and CAMx using high-time resolution data from related studies as indicated above. Again, sulfate was well reproduced, OM (OC times 1.8) was reproduced reasonably well, and nitrate and EC were overestimated by both models.

Using Atlanta Supersites Project data, Marmur et al.[340] compared source apportionment results from CMB and CMAQ. Time-series analysis of the results indicated greater daily variability by CMB than CMAQ. This variability was linked to several issues with both CMAQ and CMB. For example, CMAQ emissions inventories varied only slightly during the day, with the exception of a few major sources, and motor vehicle emissions did not reflect meteorological effects. Dust emissions appeared to be too high in the inventory and did not include daily variations because of meteorology, although CMB results suggested higher dust emissions at higher wind speeds, as one would expect.

As summarized by Russell,[336] the above performance evaluation studies, albeit limited, suggest that the following actions would improve CTM performance. Recommendations include:

- Developing better NH_3 and primary OC emissions inventories;
- Using high-time resolution data in model evaluations to allow for an improved understanding of differences between measurements and models observed throughout the day;
- Developing a better method for comparing measurements and methods at low concentrations because the model allows species to go to zero and measurement methods report lower limits of detection, thus creating a bias in the comparison at low concentrations;
- Obtaining more accurate and consistent measurements of OC, because collection and analysis methods differ across networks; and
- Including missing processes in SOA formation, especially associated with formation from biogenic emissions.

Major issues and uncertainties remaining in current PM models and their applications are summarized in Table 11.

The focus to this point has been with model performance evaluation and estimating uncertainty. However, the question remains "Do the models perform sufficiently well to be used in a regulatory setting?" Of course, this depends on two other questions: (1) "What is the best performance expected from a model?" and (2) "What level of model performance or uncertainty is acceptable for model application?" To address these questions, Boylan and Russell[343] developed a series of "goals" (the level of accuracy that is considered to be close to the best a model can be expected to achieve) and "criteria" (the level of accuracy that is considered to be acceptable for modeling applications) for PM and light extinction model performance. They then applied their approach to several modeling studies conducted over the last 10 yr or so. First, they stepped through several previous approaches and indicated the advantages to the recent approach of choice.[344] Suggested goals and criteria were then provided based on their analysis. They suggested that a proposed model performance goal has been met when both the mean fractional error (MFE) and the mean fractional bias (MFB) are less than or equal to +50 and ±30%, respectively. Additionally, the model performance is acceptable for use if the "criteria" of MFE, less than or equal to +75%, and MFB, less than or equal to ±60%, are met. Less abundant species would have less stringent performance goals and criteria. Graphical representations of results for all major PM components for 16 policy-oriented model applications are shown in Figure 10b. The goals and criteria are defined graphically in Figure 10a. It is recommended that EPA continue to establish more thorough goals and

Table 11. Major issues and uncertainties in current PM models and model applications.

Issue	Description and Significance
SOA formation	Low bias in simulated OC from current models. There is a large uncertainty in the fraction of OC from primary vs. secondary sources, and if anthropogenic SOA is significant.
Soil dust emissions	Overestimate in soil dust emissions that are not dependent upon meteorology (e.g., winds, rain). Large uncertainty in soil PM emissions levels exist.
Nucleation	Ability of three-dimensional models to capture nucleation events is poor because of both scientific uncertainties and, in some cases, lack of PM size resolution.
HNO_3 formation	Total nitrate is overestimated during the winter and underestimated during the summer, suggesting uncertainty in formation and destruction mechanisms (likely the heterogeneous formation routes and deposition rates).
Emissions	While stationary-source NO_x and SO_x emissions appear to be relatively well known, EC, NH_3, and dust appear biased and/or do not reflect daily variability. If anthropogenic SOA formation is important, then there are significant uncertainties in VOC emissions that result in SOAs.
Meteorological modeling	Meteorological models do not fully capture subsynoptic-scale variations.
Evaluation	Limited hourly data make it difficult to assess how well models capture diurnal fluctuations. Performance metrics and goals are still evolving. Evaluation procedures and goals for specific applications are not defined, nor are appropriate evaluation expectations.
Computational intensity	While PM models are becoming more computationally efficient and computers more powerful, routine use for long simulations is still demanding.

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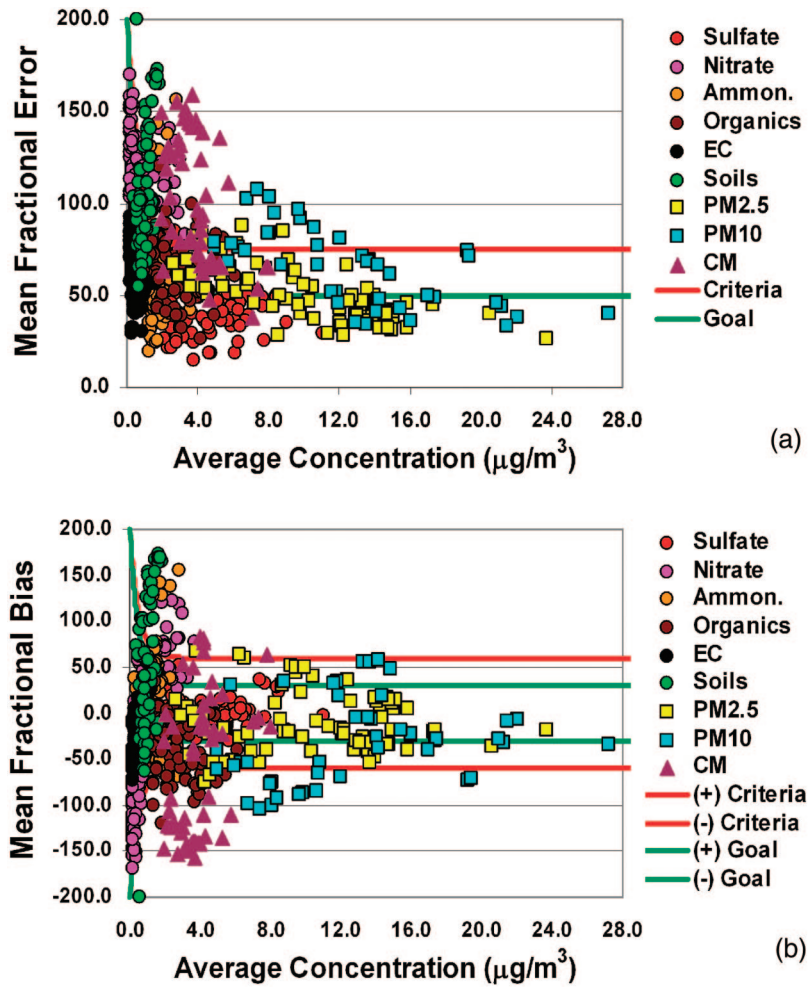

Figure 10. (a) MFE and (b) MFB as a function of concentration for 16 policy-oriented model applications.[343] Suggested criteria and goal for performance evaluation were determined from consideration of this evaluation of model performance and modeling needs. Reprinted with permission from Russell.[336] Copyright 2008 Air & Waste Management Association, *Journal of the Air & Waste Management Association*.

criteria using this model or another to provide guidance for model performance evaluations.[343,353]

Applications of Source-Oriented Models. Limited use of Supersites Program data in the application of source-oriented models on urban and regional scales has occurred to date, and thus, only a few application papers, albeit limited in scope, have been published so far in the peer-reviewed literature. VISTAS has performed preliminary modeling, but Supersites Program data were not used so those results will not be discussed here. They can be found at http://pah.cert.ucr.edu/vistas/docs.shtml. Application of CMAQ is occurring in Georgia using data collected during the Fall Line Air Quality Study, but results have not been published.[336] One limited application of a CTM using Supersites Project data occurred in Houston, TX.[179] They estimated SOA concentrations from biogenic and anthropogenic emissions, after improving the emissions inventory for biogenic species and updating the biogenic chemistry in the model. Within the urban areas, SOA was predominantly formed from industrial emissions (aromatic species reacting with OH radical), whereas north of Houston, biogenic precursors mixing with O_3 (and OH and nitrate radicals) transported from the urban area dominated the formation of SOA.

Control Strategy Relationships of Secondary PM and O_3 to Precursors. The following limited applications of source-oriented models or modules have examined the impact of specific reduction measures on PM concentrations.

PM is a complex atmospheric pollutant and control strategies to lower concentrations of one pollutant, say sulfate by reducing emissions of SO_2, may inadvertently increase another, for example, nitrate. However, as with model application, the effect of emissions controls on both PM mass, PM components, and other pollutants are just emerging. Takahama et al.[349] and Vayenas et al.[350] used reduced form TEM models to begin to understand the impact of emissions reductions in the sulfate-NH_3-HNO_3 system. For the Pittsburgh regional area, their results indicate that reductions in SO_2 could cause increases in nitrate as more NH_3 is made available to react with HNO_3. Thus, the area appears to NH_3-limited most of the time. Furthermore, their results indicate that NH_3 reductions, especially along with SO_2 reductions, would likely provide the largest decrease in

$PM_{2.5}$ mass, by reducing nitrate, ammonium, and sulfate. Gaydos et al.[291] modeled regional nucleation events that often occur in the Pittsburgh area. Their results indicate that emissions reductions in SO_2 would likely increase the number of nucleation events in the summer with decreases in the winter, whereas reductions in NH_3 would decrease the number of events in the summer and winter, with a greater impact in the summer.

Napelenok et al.[345] applied CMAQ at a 12-km grid resolution to August 1999 Atlanta Supersites Project data to examine the effect of various controls (NO_x, VOC, SO_2, and NH_3) on $PM_{2.5}$ mass and O_3. The results presented were from first-order tests with the species being controlled to 100% and only apply to summertime conditions. These results are summarized in Russell.[336] Lowering SO_2 point source emissions had little effect on O_3, but significantly reduced sulfate and ammonium, although the full benefit to $PM_{2.5}$ was not realized because nitrate increased slightly. NH_3 reductions lowered nitrate and ammonium and slightly lowered sulfate. NO_x reductions significantly reduced O_3 (primary O_3 control strategy for the southeastern United States), and also lowered concentrations of nitrate and ammonium as expected, but SOA and sulfate concentrations also were lowered. Anthropogenic VOC reductions had little impact on O_3 and $PM_{2.5}$ because in the southeast relatively little of the VOC is from these source types. Primary species (e.g., EC, primary OC, and metals) decreased on average across the domain in a linear fashion to their own emission changes, as expected.

Tsimpidi et al.[354,355] estimated the effect of uniform 50% reductions in SO_2, NH_3, VOC, and NO_x emissions on the $PM_{2.5}$ concentrations across the eastern United States. The 50% SO_2 reduction was predicted to result in an average decrease of $PM_{2.5}$ concentrations by 26% during July but only 6% during January. The smaller reduction during the winter was due to the limitation of the in-cloud formation by the H_2O_2 availability and the increase in aerosol nitrate. On the other hand, a 50% reduction of NH_3 emissions led to an average 4 and 9% decrease in $PM_{2.5}$ during July and January, respectively, by reducing mainly the NH_4NO_3. NO_x reductions were relatively efficient in reducing $PM_{2.5}$ during the summer (an average of 8%) but had only a small effect during the winter. On the other hand, anthropogenic VOCs were estimated to have a very small effect during the summer, but a much more significant impact during the winter (7% decrease of the average $PM_{2.5}$) because of their more important role in the relatively slow winter photochemistry as well as lower mixing heights. However, these are preliminary estimates, and the analysis only considered the effect on $PM_{2.5}$ mass. Before reduction strategies are developed, considerable additional modeling would be needed as well as examination of the effect of emissions reductions on other pollutants (e.g., reducing only NH_3 could result in increases in aerosol acidity).

Following the initial modeling by Tsimpidi et al.,[354,355] Pinder et al.[356] evaluated the uncertainty and cost-effectiveness of NH_3 emission reductions, relative to SO_2 and NO_x reductions, on inorganic PM in the eastern United States. They used state-of-the-science emission inventories, an emission-based regional air quality model, and an explicit treatment of uncertainty in model inputs to obtain an "NH_3 savings potential," defined as the minimum cost of implementing SO_2 and NO_x emissions controls to achieve the same reduction in ambient inorganic $PM_{2.5}$ levels as obtained from a 1-t decrease in NH_3 emissions. Results indicated a lower-bound NH_3 savings potential in the winter of $8,000 per ton NH_3, suggesting NH_3 emissions reductions to be cost-effective relative to current controls on SO_2 and NO_x sources.

Future efforts taking advantage of Supersites Program high-time resolution data by the RPOs and states, some already underway, will likely continue and increase in the near future. As noted above, major remaining uncertainties in PM modeling are listed in Table 11. Although considerable progress has been made in the last 5–10 yr in this area, considerable work is still needed, including developing improved emissions inventories for OC, EC, mobile/area NO_x, VOC, and NH_3 and obtaining accurate meteorological fields on an hourly or better time frame. Considerable efforts are needed to ensure the models are correctly simulating SOA and the partitioning of sulfate, nitrate, and ammonium. More work is needed to be sure the models are correctly apportioning primary versus secondary and anthropogenic versus biogenic fractions of OC. Nucleation is not well simulated in the models, and there may be a lack of scientific foundation in the models to address this recently identified issue.

EMISSIONS: ESTIMATES, INVENTORIES, AND UNCERTAINTIES

Measuring emissions from sources and developing emissions inventories were not specific objectives of the Supersites Program. However, measuring and estimating source emissions are critical components to understanding the accumulation of PM on urban and regional scales. Emissions estimates or inventories are fundamental inputs to CTMs, which simulate the processing of those emissions through the atmospheric system. Inventories also provide clues to the most important sources of PM within a given area and allow for tracking of trends and variability of sources. Emissions estimates and inventories only provide information on directly emitted gases and particles (primary emissions). Primary emissions are from anthropogenic and natural sources. Primary particles, as emitted from sources, include all size ranges from the smallest UF PM to particles much larger than 10 μm in diameter. They also have a wide range of chemical compositions, but do not usually contain nitrate and sulfate to any great extent because these are mostly secondary species. There can also be significant source-to-source variability in emissions. This variability is due to differences in processes leading to the emissions. For example, industrial source emissions likely depend on the operational needs of the industry, whereas natural emissions from plants or soil depend on meteorological factors; for example, temperature, RH, and other factors.

Realizing the importance of emissions estimates to the overall goal and objectives of the Supersites Program, several of the Supersites Projects directly included emissions measurements in their efforts. In addition, the

science/policy relevant questions for the Supersites Program Synthesis included a specific question related to emissions estimates and uncertainty in those estimates—Q16, Table 3. Key findings from Simon et al.[338] are provided below, followed by a brief summary of direct emissions measurements or indirect emissions estimates conducted as part of the Supersites Program with either direct funding or supplemental funding.

Simon et al.[338] examined uncertainty in emissions inventory estimates by comparing emissions inventory estimates, as the fraction of primary $PM_{2.5}$ emitted in a source region (bottom-up emissions estimates), to estimates of source strengths determined by source apportionment analyses (top-down emissions estimates). These comparisons were obtained at Supersites Project locations in Houston, TX; Atlanta, GA; Baltimore, MD; Fresno, CA; Los Angeles, CA; Washington, DC (adjacent to Baltimore); and a few other locations depending on the emissions category. Six source categories for primary $PM_{2.5}$ emissions were included in the analysis by Simon et al.[338]: on-road sources, non-road sources, cooking, biomass combustion, fugitive dust, and point sources. Precursor species emissions were limited to NH_3 because uncertainty in NH_3 emissions estimates are considerable, whereas those for NO_x and SO_x emissions are relatively small, and because a review of VOC emissions would warrant its own review because of the large number of species and wide range of source categories. A summary of the inventory estimates and source apportionment results presented in Simon et al.[338] is given in Table 12.

Lane et al.[357] evaluated the primary carbonaceous aerosol emissions inventories in the eastern United States during a summertime episode in mid-July 2001. Simulations were performed using a source-resolved CTM (described below) to track primary OM and EC concentrations for eight different specific sources: gasoline vehicles, non-road diesel vehicles, on-road diesel vehicles, biomass burning, wood burning, natural gas combustion, road dust, and all other sources. In the source-resolved approach, primary OC from each source category was modeled independently by separating emissions inventories into subcategories. The results were compared with the results of CMBs for Pittsburgh, PA, and multiple urban/rural sites from the SEARCH network. Significant discrepancies were found between the source-resolved model and the CMB model predictions for some of the sources. For example, the source-resolved model predicted EC concentrations that were much higher than measurements from the STN network. Non-road diesel, according to the emission inventory, was predicted to contribute more to EC in urban areas than on-road diesel. These results suggested that both the on-road and non-road diesel emissions inventories were overestimated and may need to be reduced. Natural gas, wood burning, and biomass burning were other sources that had emission inventory problems. These results suggested that the primary OM emission inventory for natural gas should be reduced by at least 50 times its current inventory value. The contribution of primary OM and EC from wood burning was too high along the U.S. northeastern coast, predicting average primary OM concentrations greater than 0.5 $\mu g/m^3$. Primary OM contributions from biomass burning were overestimated in Texas.

Emissions inventory data (bottom-up estimates) are typically estimated from emissions factors and activity data. Emissions factors are often based on a limited number of source tests within a source category and within a limited number of areas; for example, maybe just within Los Angeles, CA, and may vary significantly from source to source even within a given source category.[358] Emissions factors also may be out of date because sources change over time, due to, for example, better emissions controls or changes in feedstock. National Research Council (NRC)[359] and NARSTO[360] also pointed out the need for not only having speciated emissions factor data but also size-resolved chemical component data. New studies are obtaining emissions data from a variety of sources in more locations allowing regional differences to be observed with regionally specific emissions estimates included in air quality modeling exercises. Speciated size-resolved information is beginning to be collected.[361]

Clearly, from the results presented in Table 12 and in more detail by Simon et al.[338] and Lane et al.,[357] considerable uncertainty and variability exist in both the bottom-up and top-down emissions estimates. A factor of 2 or more uncertainty in emissions estimates can be realized in any of the categories examined with even greater uncertainty in emissions factor measurements and calculations. Variability in published source profiles (e.g., marker-to-OC ratios), including photochemical oxidation of those markers in the ambient air, creates up to a factor of 5 or more uncertainty in CMB results.[207–209,235,313] These uncertainties are due, in a large part, to a very limited number of emissions measurements (factors and activity data), the representativeness of the measurements themselves, and the fact that emissions vary because of many factors, including, for example, location, control technology, and meteorology.

As part of the Supersites Program and related field studies, direct emissions measurements (bottom-up approach) based on real-world sampling rather than laboratory measurements were obtained for emissions from motor vehicles, an industrial coke plant, and biogenic emissions (wildfires). Indirect emissions estimates, combining bottom-up and top-down approaches, were obtained for motor vehicle emissions, a variety of industrial sources, and biogenic emissions, by modeling efforts using ambient data either for verification or by inverse modeling approaches.

Motor vehicle emissions measurements were made in tunnel studies in Houston, TX,[362,363] and Pittsburgh, PA.[364] In each case, fuel-based emissions factors (mass emitted/mass fuel burned) were developed. This approach is believed to vary less over the full range of driving conditions (e.g., vehicle attributes, operating mode) than emissions factors based on vehicle distance traveled (mass emitted/distance).[365] The Houston tunnel studies obtained estimates for gaseous species (CO, NO_x, nonmethane hydrocarbons [NMHC])[362] and $PM_{2.5}$.[363] The NMOC emissions factor was slightly higher than ones obtained in previous studies conducted at least 5 yr earlier, suggesting the current Houston fleet was comprised of older, less

Table 12. $PM_{2.5}$ primary emissions inventory (EI) estimates by Supersites Project region using results from the Supersites Program and related studies (primarily synthesized from Simon et al.[338]).[a,b]

Source Category	Location	Inventory Estimates: NEI[494] (%)			Source Apportionment Estimates (%)	Reference (source apportionment)	Comments: Most NEI data cover the time period from ~1990 to 2000 unless noted
		On-road	Non-road	On-road and non-road	On-road and non-road are usually not separated		Percentages of $PM_{2.5}$ exclude the fugitive dust portion of these emissions, unless noted, because fugitive dust comprises a significant portion (NEI estimate is 89%) of these emissions
On-road and non-road[b,c]							
	California	12	14	26			
	SJV				~26 (winter)	Vickery[165]	
	Fresno			8	12–50	Schauer and Cass,[62] Christensen,[495] Magliano, et al.,[496] Held et al.,[497] Zhao and Hopke[498]	Diesel estimated as 58–82% of mobile source apportionment
	Los Angeles			18 (62% of this from diesel)	28–68	Schauer et al.,[499] Vickery,[165] Mysliwiec and Kleeman,[500] Held et al.,[497] Schauer et al.,[61] Zhao and Hopke[498]	Diesel estimated as 55–94% of mobile source apportionment
	Texas/Missouri	8	13	21			
	Houston				25–33	Fraser et al.[394]	
	New York/ Pennsylvania/ Maryland	10	11	21			
	Philadelphia				76–88	Vickery[165]	May not have included other primary sources and thus maybe overestimated
	Pittsburgh				13–20 (winter) 5–31 (summer)	Subramanian et al.[208]	Fraction of ambient OC; gasoline-diesel split more variable and depends on source profiles used in CMB
	Baltimore			12 (31% gasoline, 69% diesel)	38–71 (79–98% attributed to gasoline)	Chen et al.,[501] Song et al.,[502] Kim and Hopke,[503] Begum et al.,[504] Ogulie et al.[493]	Split between gasoline and diesel motor vehicle emissions contributions are considerably different between inventory and source apportionment
	Georgia	5	6	11			
	Atlanta			7–16[#]	48–64	Kim et al.,[480] Zheng et al.[60]	[#]Including dust; 66–75% from diesel engines
	National average	4[507,#]	8[507,##]	12	31–74	Kim et al.,[310,479,480] Zheng et al.,[60] Marmur et al.,[340,405] Liu et al.[506]	[#]On-road, national average with fugitive dust 34%, 89.5% of which is fugitive dust[507] [##]Of the 8%, 15% is from gasoline and 60% is from diesel motor vehicles

Table 12. (cont.)

Source Category	Location	Inventory Estimates: NEI[494] (%)	Inventory Estimates: Other Inventory (%)	Source Apportionment Estimates (%)	Reference (source apportionment)	Comments: Most NEI data cover the time period from ~1990 to 2000, unless noted
Cooking[d,e,f]	California		4.4 (Simon et al.[338] CARB[508])			
	Fresno		2.1 (Simon et al.[338] CARB[508])	13 (meat cooking)	Held et al.[497]	
	Los Angeles		8.8 (Simon et al.[338] CARB[508])	2–21	Schauer et al.,[499] Held et al.,[497] Schauer et al.,[61] Zhao and Hopke[498]	
	Texas/Missouri			10–20	Fraser et al.[394]	
	Houston area		10–15 (of $PM_{2.5}$ mass)	10–20; 6 for meat cooking	Fraser et al.[394]	
	Pittsburgh			10%, study average	Robinson et al.[206]	
	Atlanta		5 (Marmur et al.[340])	5, up to 15 (summer)	Zheng et al.[60]	
	National average					
Residential fuel combustion[f,g]	California	18	14.7 (Simon et al.[338] CARB[508])[#]			[#]95% of residential fuel combustion from wood[338]
	SJV			32	Vickery et al.[165]	Vegetative burning, autumn
	Fresno	5[#]	9.8 (Simon et al.[338] CARB[508])	36–65 (peaks in winter)[##]	Schauer and Cass,[62] Christensen, [495] Magliano et al.,[496] Held et al.[497]	[#]Total wood smoke and vegetative burning is 48% [##]Wood smoke and vegetative burning, residential not distinguished
	Los Angeles	10	5.7 (Simon et al.[338] CARB[508])	1–29[#]	Schauer et al.,[61,499] Held et al.,[497] Zhao and Hopke[498]	[#]Varies by location within South Coast Air Basin, includes a 1982 study[61]
	Texas/Missouri	14				
	Houston			1–2	Dennis et al.,[509] Junquera et al.,[373] Buzcu et al.[489]	
	New York/Pennsylvania/ Maryland	17				
	Pittsburgh			14.5 (fall) 10.5 (winter)	Robinson et al.[209]	Percentage of ambient OC
	Baltimore/ Washington, DC	13		5–36	Chen et al.,[501] Begum et al.[504]	
	Georgia	7				
	Atlanta	3–6 (Marmur et al.,[505] including dust)		8–46[#]/15 (summer); 46 (winter)	Kim et al.,[310,479,480] Marmur et al.,[340,505] Liu et al.,[506] Zheng et al.[60]	[#]Apportioned to wood smoke
	National average	11 (EPA[507])				

Table 12. (cont.)

Source Category	Location	Inventory Estimates: NEI[494] (%)	Inventory Estimates: Other Inventory (%)	Source Apportionment Estimates (%)	Reference (source apportionment)	Comments: Most NEI data cover the time period from ~1990 to 2000, unless noted
Wildfires, prescribed burning, other outdoor fires[f,g] (Also see residential fuel combustion)	Los Angeles			1–2	Schauer and Cass[62]	
	Texas			1–2	Dennis et al.,[509] Junquera et al.[373]	
	Pittsburgh[#]			14.5 winter[##] 10 fall 2 summer and summer		[#]Biomass burning was apportioned with no distinction between residential biomass fuel combustion and the wildfire source category [##]Upper limit with an uncertainty of 2 or more because of source profile variability
Fugitive dust[h] (road dust and other)	California					
	Fresno	32		1–13	Schauer and Cass,[62] Christensen,[495] Magliano et al.,[496] Held et al.[497]	
	Los Angeles	34		14–40[#]	Schauer et al.,[61,499] Held et al.,[497] Zhao and Hopke[498]	[#]14–46% of fugitive dust from local soil rather than road dust,[497,498] although some fraction may be Asian dust[498]
	Texas/Missouri					
	Houston			2 or less depending on location	Buzcu et al.,[391] Yue and Fraser[233]	
	Washington, DC/ Baltimore/ Maryland metro area	33		6–20[#]	Song et al.,[502] Kim and Hopke,[503] Begum et al.[504][##]	[#]15–56% of fugitive dust is soil dust [##]At least part of the soil dust fraction likely comes from Asian and Saharan dust storms[503,504]
	Georgia/Atlanta	28–45		3–15	Kim et al.,[310,479,480] Marmur et al.,[340,505] Liu et al.,[506] Zheng et al.[60]	
	National average[i]	41 (EPA[507])				21% paved roads, 52% unpaved roads, 23% construction, 4% other
Point sources[j]	California	10				
	SJV			43 (unknown source category)	Vickery[165]	In source-apportionment studies point sources are often embedded in one other or unknown

Table 12. (cont.)

Source Category	Location	Inventory Estimates: NEI[494] (%)	Inventory Estimates: Other Inventory (%)	Source Apportionment Estimates (%)	Reference (source apportionment)	Comments: Most NEI data cover the time period from ~1990 to 2000, unless noted
Point sources[j] (cont.)	Los Angeles			17–55 (other sources)[#]	Schauer et al.,[499] Vickery[165]	[#]NEI estimated 15% of primary $PM_{2.5}$ emissions associated with industrial and incineration[494]
	Texas/Missouri	19				
	New York/ Pennsylvania/ Maryland	37				
	Washington, DC/ Baltimore/ Maryland metro area	16 (industrial and electric utilities) plus 14 (incineration and open waste burning)		3–14[#] plus 10–23[##]	Song et al.,[502] Kim and Hopke,[503] Begum et al.,[504] Ogulei et al.[493]	[#]Heavy oil combustion associated with industrial and electric utilities emissions; apportionment higher in winter than summer [##]Incineration and open waste burning
	Georgia	17				
	Atlanta			16–21	Kim et al.,[480] Zheng et al.[60]	10% of primary $PM_{2.5}$ due to metal processing, asphalt manufacturing, cement kiln[62,310,340,479,480,505,506]
	National average	18				Of which electric utility (20%—coal represents 80–90% of utility $PM_{2.5}$ emissions), industrial fuel combustion (22%), metals processing (17%), mineral products industry (15%), other (10%)
Sea salt	Los Angeles			1–18	Held et al.,[497] Zhao and Hopke[498]	
	Baltimore			6–15	Song et al.,[502] Kim and Hopke,[503] Begum et al.,[504] Ogulei et al.[493]	
NH_3		**NH_3 emissions by source (%)**				
	Texas		80 (livestock) 8 (fertilizer and agricultural crops) 5 (scrubland and grassland) 2 (on-road vehicles) 4 (other) (Anderson et al.,[510] Corsi et al.[511])		Pavlovic[395]	

Table 12. (cont.)

Source Category	Location	Inventory Estimates: Percent of NH_3 Emission by Source	Inventory Estimates: Other Inventory (%)	Source Apportionment Estimates (%)	Reference (source apportionment)	Comments: Most NEI data cover the time period from ~1990 to 2000, unless noted
NH_3 (cont.)	National average	74 (livestock) 13 (agricultural crops) 5 (on-road vehicles) 3 (agricultural chemicals) 2 (waste disposal and recycling)	85 (animal husbandry and fertilizer application) (Gilliland et al.[512])	Bias between modeled[#] and ambient was 25–50% (root mean square error)	Gilliland et al.[512]	[#]NEI (modified) as input to regional photochemical grid model and comparison between modeled NH_3 and ammonium to ambient data

Notes: [a]Simon et al.[338] examines uncertainties in emissions estimates by comparing inventory data to ambient source-apportionment results (top-down evaluation) and summarizes source types, emissions estimation methods and magnitude (bottom-up evaluation), composition, size distributions, and regional comparisons of estimates with observations (results summarized within this table) for each of the source categories listed in the first column of this table. [b]Percentages to $PM_{2.5}$ excluding the fugitive dust portion of these emissions, unless noted, because fugitive dust comprises a significant portion (NEI estimate is 89%) of these emissions. [c]Primary mobile source (on- and non-road) emissions inventory (EI) estimates are typically by two methods: vehicle miles traveled and fuel consumption (fuel-based). Limited comparison studies between these two methods indicate a variation in on-road mobile source estimates by a factor of 2–4. Primary $PM_{2.5}$ tire and break wear EI estimates may have uncertainties up to a factor of 10 (Simon et al.[338]). [d]Considerable uncertainty exists in the source-apportionment estimates for cooking when using K^+ (water-soluble K) as a tracer because K^+ emissions from wood smoke are equal to or up to 3 times greater than that from cooking. Organic tracers may provide improved estimates (EC and levoglucosan for wood smoke; palmatic and oleic acids for cooking). [e]CARB and EPA emissions factors are similar (Simon et al.[338]). [f]Distinguishing between different biomass burning sources (residential, wildfires, prescribed and agricultural burning, and other fire types) is difficult because of the limited number of species available as possible tracers for these similar source types. [g]Variability (size, location, frequency, duration) in biomass combustion sources, such as wildfires, prescribed burning, and other outdoor fires, adds considerable uncertainty to EI estimates of residential fuel combustion (mostly wood burning); thus, source-apportionment results should be viewed as an upper bound for these sources (Simon et al.[338]). [h]Fugitive dust comes from many sources; for example, paved and unpaved roads, construction, wind blown dust from managed and natural soil surfaces, and industrial and agricultural sources. As with fires, fugitive dust emissions are variable and depend on numerous factors that vary by location, season, and soil type to note a few examples. [i]Malm et al.[513] noted that at many IMPROVE sites located across the United States, large increases in fugitive dust in April could be attributed to long-range transport of African and Asian dust. Winter concentrations were typically low at most sites, with estimated highest ambient concentrations in the southwestern United States. [j]Considerable regional variability in emissions because of individual industrial categories being centered in specific regions of the country; for example, petroleum in southeastern Gulf Coast region, and coal-fired power plants in ORV. NEI = National Emissions Inventory.

well-maintained vehicles. NO_x and CO emissions estimates were comparable to previous studies. $PM_{2.5}$ emissions estimates were based on gaseous and particulate phase sampling within the tunnel, followed by CMB modeling that included inorganic and organic species source profiles. Separate diesel and gasoline fuel-based emissions factors were developed. The diesel emissions factor was approximately 20 times higher than that obtained for the gasoline factor (3.3–3.4 vs. 0.15–0.18 g $PM_{2.5}$/kg of fuel burned) with small differences seen between midday and afternoon sampling.

The tunnel study in Pittsburgh, PA,[364] determined fuel-based emissions factors for PM and major and minor chemical components (see Table 3 in Grieshop et al.[364]). The emissions factors of NO_x, $PM_{2.5}$, EC, OC, and trace metals varied with operating conditions and fleet composition. For example, the emissions factor for heavy-duty diesel vehicles was approximately 30 times higher than that obtained for light-duty vehicles (1.1 ± 0.16 vs. 0.03 ± 0.04 g $PM_{2.5}$/kg of fuel burned); a similar ratio to that observed in Houston, TX, but the overall emission rates in Pittsburgh, PA, are about a factor of 3 lower. Emissions of brake wear species (i.e., Cu, Sb, barium [Ba], and gallium [Ga]) were highest during rush hour. A seasonal shift in average OC/EC ratio also was observed; fall and summer OC/EC ratios were 1.07 ± 0.6 and 0.26 ± 0.06, respectively, during light-duty vehicle dominated periods. Potential causes for this shift are increased partitioning of SVOCs into the gas phase during the summer months and/or effects of seasonal changes in fuel formulation.

"Chase" studies, using an instrument-equipped vehicle following other motor vehicles in real-world sampling, were conducted in NYC.[366–368] The primary purpose of these studies was to examine differences in the emissions of SO_2, formaldehyde, methane, NO_x, and nonrefractory PM_1 ($NRPM_1$, $PM_1 < 1$ μm in diameter) mass and $NRPM_1$ composition from public buses using different control technology, including new and old diesel engines, diesel with continuously regenerating technology (CRT), ultralow sulfur diesel, and compressed natural gas (CNG). Low-sulfur fuel resulted in lower (by a factor of 16) sulfur emissions, whereas use of CNG resulted in higher emissions of formaldehyde and methane than found in standard diesel buses. The NO_x emissions from the diesel and CNG buses were comparable, but the NO_2/NO_x ratio increased for CRT-controlled buses. $NRPM_1$ was obtained using an AMS that provided size and chemical composition data. The diesel exhaust in the PM_1 size range appeared to be dominated by lubricating oil emissions. Newer buses emitted less $NRPM_1$ than older

buses, and CRT-equipped and CNG-equipped buses have similar $NRPM_1$ emissions, which were approximately 60% less than the buses with new engines. These finding suggest control strategy approaches for reducing pollutants from diesel vehicles; however, a balance will be needed among the control measures and the different pollutants of interest and that multipollutant effects should be considered.

In Los Angeles, CA, inverse modeling was used to develop road and grid-level distance- and fuel-based size-resolved particle emissions factors near highways and at a 1-km distance (CTM scale in urban areas).[287] Measurements by Zhu et al.[273–275] were used in the analysis and included summer and winter sampling at the 405 and 710 freeways, the latter with a higher proportion of heavy-duty diesel traffic. The total particle number emissions factor is in the range of 10^{13}–10^{14} particles/km-vehicle, similar to previous studies. Emissions rates also were estimated, albeit with greater uncertainty, at 133 and 21 mg/km-vehicle for trucks and non-trucks, respectively. Seasonal shifts in the size mode of the emissions particle distributions were also observed.

$PM_{2.5}$, PM_{10}, and gaseous emissions profiles (mass of species of interest/$PM_{2.5}$ emitted in percent) were obtained at a large metallurgical coke production facility.[369] Fence line monitoring was used because of large amounts of fugitive emissions and the many emissions sources associated with these sorts of facilities. Tables 3 and 4 in Weitkamp et al.[369] present the $PM_{2.5}$ and gas-phase species emissions profiles, respectively. The major components of the emissions profile (in percent of $PM_{2.5}$ emitted) are OC (40%) and EC (25%). Significant contributions from As, Zn, Se, and Pb also were noted, although each was well less than 1%. The $PM_{2.5}/PM_{10}$ ratio was 0.84.

$PM_{2.5}$ source profiles were developed for urban and rural road dust and leaf abrasions as part of the Pittsburgh Supersites Project. The urban road dust was enriched in metals associated with anthropogenic sources such as Fe, Zn, Cu, Pb, Cr, Ni, molybdenum (Mo), Sb, and organic species associated with primary emissions.[370]

High-time resolution trace element measurements using SEAS[153,154] combined with meteorological variables and PDRM modeling[157,304] or time-series derived ratios[156] were applied to obtain relative emissions profiles from a series of combustion sources in Tampa, FL, as part of the BRACE study. The SEAS and PDRM analyses were described earlier and used here to obtain emissions rates of SO_2, and trace elements from industrial sources and power plants.[157,304] Accuracy against known emissions was within 10%. The ratio method provided relative concentration profiles (mass species/mass tracer element) referenced to a source marker element because $PM_{2.5}$ mass was not available.[156] Principal component analysis and PMF were used to separate overlapping sources in these data. Profiles generated by PMF also agreed well with those obtained by the ratio method. Tables 2 and 3 in Pancras et al.[156] provide source profiles for an animal feed supplements production facility and an incinerator. Emissions profiles for these sources were obtained although each source was greater than 15 km away from the sampling site that was situated in an area with many possible source impacts. Four other sources were discussed.

Biogenic emissions estimates were obtained for wildfires and sesquiterpene, the latter a primary pollutant that is a precursor for secondary OC formation. Sesquiterpene emissions fluxes (kg C/km^2-hr) were estimated in the Houston-Galveston area in southeast Texas[241] using a modified version of the Global Biosphere Emissions and Interactions System (GloBEIS).[371,372] This bottom-up approach used a land cover database that included more than 600 species at a 1-km spatial resolution. Estimated fluxes were between 0.07 and 0.65 kg C/km^2-hr. Fluxes at the lower end of the range were consistent with contemporary carbon estimates for the area.[212] As discussed earlier in this paper, these results were also used to estimate SOA from sesquiterpene in the Houston-Galveston area.

Wildfire emissions estimates were obtained in southeastern Texas and in Baltimore, the latter because of the impact of the wildfires in Quebec, Canada during July 2002.[373] In Texas, emissions were based on a bottom-up calculation that included acreage burned, fuel loading, and fuel emissions factor models. On days with the highest wildfire activity during August and September 2000, estimated emissions were 3700 t of CO, 250 t of VOC, 340 t of $PM_{2.5}$, and 50 t of NO_x. On these days, the estimated CO and VOC emissions from the fires exceeded light-duty gasoline vehicle emissions in the Houston area. Ambient concentration estimates based on application of the emissions predictions and air quality modeling were within a factor of 2 of values observed by aircraft.

Park et al.[191] used the slope of the EC/CO ratio from the ambient data after background subtraction, a CO emissions factor obtained from the literature, and the area burned to obtain an estimate of EC emissions from the Quebec, Canada wildfire episode. Park et al.[191] estimated that 4.75 Gg of EC were emitted during these fires, which represented approximately 50% of the average boreal fire emissions in Canada each year (~9.94 Gg EC).

SUPPORTING STATE IMPLEMENTATION PLANNING

State agencies and RPOs have used data from the Supersites Program and related studies to support the development of SIPs for $PM_{2.5}$ to address the current PM NAAQS and for regional haze to address current regional haze rules. This use includes a variety of receptor-oriented and source-oriented approaches as discussed in a previous section. Summarized here is information provided by Supersites Program PIs, state agency personnel, or RPO personnel indicating what information has already provided guidance for SIP development (state agency or RPO personnel) or has been provided (Supersites Program PIs) in support of state agencies and RPOs in their efforts to reduce PM to levels below NAAQS or Regional Haze Rules.

Table 13 summarizes the limited information received to date regarding use of data from the Supersites Program and related studies for supporting development of emissions reduction strategies for either $PM_{2.5}$ or regional haze (the latter the main focus of RPO efforts). Table 13 provides a listing of these studies by region; area of application; measurement method/species, air quality data, model (as applicable), and relevant references. The published papers cited are typically

Table 13. Application of Supersites Program data in support of SIPs by U.S. regions (as of mid-2006).

Region Supersites Project and Related Studies Information Supported	Area of Application	Measurement Method/ Species, Air Quality Data if Not Direct Supersites Project Data, and Model (as applicable)	References[a]
Atlanta, GA and southeastern United States, including RPO (VISTAS) studies	Model evaluation	CMAQ applied to 1999 Atlanta, July 2001, and/or January 2002 sampling periods over the southeastern United States, various data sources and OC speciation data collected at eight SEARCH sites July and October 2000 and January 2002 (Zhang et al.[348])	Hu et al.,[379] Napelenok et al.,[345] Chang,[514] Morris et al.,[346,347] Boylan and Russell,[343] Russell,[336] Bhave et al.[375] Zhang et al.[515–517]
	CTM source characterization and sensitivity testing	CMAQ applied to 1999 Atlanta and July 2001 and January 2002 sampling periods, various data sources	Hu et al.,[379] Napelenok et al.,[345]
	Emissions inventory	Urban-to-Regional Multiscale Model (URM) (Kumar et al.,[518] May and July 1995); CMAQ	Mendoza-Dominguez and Russell,[378] Bhave et al.[375]
	Process modeling issues	Various, Supersites Project and related studies (Pittsburgh and southeastern United States)	Takahama et al.,[349] Vayenas et al.,[350] Park et al.,[139,161,341]
	Identifying source apportionment uncertainties	CMAQ, CMB; July 2001, January 2002	Marmur et al.,[340] Park et al.,[139] Boylan and Russell,[343] Bhave et al.[375]
	Model application (including initial source contribution estimates and preliminary testing of emissions reduction strategies and impact on pollution levels)	CMAQ applied to 1999 Atlanta and July, 2001 and January, 2002 sampling periods, various data sources	Hu et al.,[379] Morris et al.,[347] Chang,[514] Napelenok et al.,[345] Russell[336]
Mid-Atlantic Region (MARAMA) ($^{+}$Identified specifically by MARAMA[381,538]			
NYC	Methods evaluations—filter-based	$PM_{2.5}$ Mass (e.g., FRM)$^{+}$	Schwab et al.,[34] Rees et al.[90]
Pittsburgh, PA	Methods evaluations—continuous	$PM_{2.5}$ Continuous (various TEOMs, BAM)	Schwab et al.,[34] Rees et al.,[90] Khlystov et al.[119]
		Composition—nitrate, sulfate, size distribution (3 nm to 2.5 μm), OC, EC, SOA, PBW, light scattering^{+}	Wittig et al.,[125] Stanier et al.,[117,279] Polidori et al.,[382] Cabada et al.,[177,519,183] Khlystov et al.[102]
	Characterization—spatial	$PM_{2.5}$, sulfate, and OC; regional variation^{+}	Tang et al.[182]
	Characterization—temporal	$PM_{2.5}$ (OC, sulfate)$^{+}$	Rees et al.,[90] Wittig et al.[125]
	Characterization—diurnal	Nitrate/HNO_3; sulfate^{+}	Wittig et al.[125,175]
	Characterization—size distribution chemistry	Sulfate, nitrate, ammonium^{+}	Cabada et al.[177]
	Meteorological aspects	PM episode drivers^{+}	Modey et al.[217]
	Model evaluation	CAMx, July 2001; July, October 2001, January, April 2002	Gaydos et al.,[291,352] Karydis et al.[351]
	Emissions inventory	CMB-CMAQ primary OC, NH_3, EC tracer and CMB	Lane et al.,[357] Pinder et al.,[520] Cabada et al.[521]
	Process modeling issues	TMR; GFEMN; ISORROPIA, AIM; nucleation (NH_3-H_2SO_4-water system)	Stanier et al.,[357] Takahama et al.,[254,349] Vayenas et al.,[350] Jung et al.[283]
	Receptor-oriented source contribution estimates including impact of long-range transport of PM and PM precursors	PM mass and composition—SOA, VOC/OC/SOA, UF PM composition; size distribution, size distribution and chemistry	Cabada et al.,[177,183,521] Millet et al.,[187] Polidori et al.,[382] Tang et al.,[182] Zhou et al.,[318,319,323] Maranche[522]
	Receptor-oriented source contribution estimates (UF PM, including nucleation events)	PMF, size distribution, size distribution and chemistry	Gaydos et al.,[291] Stanier et al.,[278,279] Zhou et al.[318,319,323]
	CTM source contribution estimates	CAMx, (eastern United States and the Midwest)	Lane et al.,[357] Gaydos et al.,[352] Karydis et al.[351]
	Control strategy implications (modeled results—receptor-oriented, EC tracer or TEM, CTM—suggesting which species to reduce emissions to obtain ambient concentration reductions)	NH_3, SO_2; OC-SOA, NH_3-H_2SO_4-water system and nucleation bursts; PBW; size distribution, size distribution and chemistry	Cabada et al.,[183] Gaydos et al.,[291] Jung et al.[283] Khlystov et al.,[119] Maranche,[522] Millet et al.,[187] Polidori et al.,[382] Rees et al.,[90] Takahama et al.,[349] Vayenas et al., [350] Zhou et al.[318,319,323]
	Conceptual model		MARAMA,[381] NESCAUM[523]

Table 13. (cont.)

Region Supersites Project and Related Studies Information Supported	Area of Application	Measurement Method/ Species, Air Quality Data if Not Direct Supersites Project Data, and Model (as applicable)	References[a]
St. Louis, MO and upper Midwest (identified specifically by LADCO-Midwest RPO, July 2006[537])	Receptor-oriented source contribution estimates	PMF, ME, CMB, CPF, PSCF	Lee et al.,[327] LADCO,[328] Brown et al.,[385] Bae et al.[524]
	Model evaluation	CTM	Ongoing[537,539]
	Control strategy implications	Primary OM	Brown et al.[385]
Houston, TX, and southeast Texas	Organic speciation/^{14}C	PM mass and composition, OC species by extraction and GC-MS; VOC (GC-FID); 1997/1998 and 2000 (TexAQS)	Fraser et al.,[59,394] Yue and Fraser,[63,233] Lemire et al.,[212] Zhao et al.[399]
	Emissions inventory (wildfire, gasoline, diesel, biogenic SOA, reactive VOC)	CAMx, GloBEIS, CMB, gas and aerosol composition, LIDAR, aircraft, reactive VOC; NH_3	Junquera et al.,[373] Fraser et al.,[363,393] Garnes and Allen,[74] Vizuete et al.,[241] Ryerson et al.,[397] Pavlovic et al.[395]
	Modeling and atmospheric processes/process modeling issues to assess mechanisms	CAMx; SAPRC with modified chemistry; supporting CAMx—PMF and CMB; FAC; NH_3; size distributions and hygroscopicity (DMA-TDMA)	Junquera et al.,[373] Buzcu et al.,[525] Nopmongcol and Allen,[392] Dechapanya et al.,[388,389,390] Russell and Allen,[179] Pavlovic et al.,[395] Gasparini et al.[293]
	Receptor-oriented source-contribution estimates	CMB (molecular markers) (general apportionment and diesel/gasoline MV in tunnel); CPI[b]; FAC[c]; ^{14}C	Allen and Fraser,[386] Fraser et al.,[59,363,394] Yue and Fraser,[63,233] Buzca and Fraser,[525] Buzca et al.,[391] Lemire et al.[212]
	Ozone formation and accumulation	CAMx, CMB-ME (wind speed and WD, temperature, weekend/weekday); NNLS[d]	Tanaka et al.,[401] Chang and Allen,[402,403] Gan and Hopke,[398] Zhao et al.,[399] Kleinman et al.,[396] Ryerson et al.[397]
Fresno, CA, and Central California	Methods evaluations—filter-based and continuous	Mass, OC, EC, nitrate, size distributions	Watson and Chow,[140] Chow et al.,[32,49,407,526] Park et al.[139]
	Characterization—spatial and temporal	Mass, NH_4NO_3; OC; EC, BC, light scattering; PAH, OC species	Chow et al.,[32,38,49,407,408] Watson and Chow,[194] Rinehart et al.,[409] Turkiewicz et al.,[169] Park et al.,[139] Watson et al.,[6] Hering et al.[410]
	Characterization—size distribution	Nanoparticle (3–10 nm), UF PM (<100 nm), accumulation mode (0.1–2 μm)	Watson et al.,[280,281,282] Hering et al.[527]
	Meteorological factors influencing PM accumulation	Mass and major components, seasonal difference summer and winter	Watson and Chow,[194] Watson et al.,[282] Chow et al.,[407,408] Turkiewicz et al.,[169] Park et al.[139]
	Model performance evaluation	Supersites Program data	SJVAPCD[405,406]
	Receptor-oriented/data analysis source-contribution estimates	PM mass and chemical composition using filter-based and continuous methods	Rinehart et al.,[409] Watson et al.,[6,280] Watson and Chow,[194] Chow et al.[408]
	Indoor and outdoor—measurements and characterization to support exposure studies, such as FACES and FI/OES[e]	Time and chemically resolved PM mass and composition	Tager et al.,[411] Lunden et al.[412,528]
	Control strategy assessment/model application	Supersites Program data	SJVAPCD[405,406]
	Conceptual model	Episode characterization	Watson et al.,[6] Turkiewicz et al.,[169] Watson and Chow[194]
EPA, national and various regions	Model evaluation and preliminary application	Data from multiple Supersites Projects	Dennis[546]

Notes: [a]Not a comprehensive listing, but those references identified as most supporting states and RPOs in understanding factors controlling PM accumulation in their region and source contributions at receptor sites. GFEMN = Gibbs Free Energy Minimization Model, SARPC = Statewide Air Pollution Research Center. [b]CPI = carbon preference index—organic species in plant waxes are enriched in odd-carbon-number *n*-alkanes; petroleum-derived alkanes are not enriched. [c]FAC = fractional aerosol coefficients—used to estimate SOA yields from emissions in the inventory; used in CTM. [d]NNLS source apportionment method described in the source contribution section. [e]FACES and FI/OES = Fresno Asthmatic Children's Environment Study and the Fresno Indoor/Outdoor Exposure Study.

discussed in more detail in the earlier sections of this paper. Results from gray literature reports are typically not described here unless they are described in one of the technical papers supporting the synthesis,[374] because most represent preliminary results and have not been peer-reviewed. However, details of these studies and results can be found in the cited gray literature references.

By Region of the Country

Atlanta, GA, and Southeastern United States. In the southeastern United States, data from the Supersites Program

and related studies were used to evaluate CTMs (CMAQ and CAMx), to compare CTMs to CMB models, and to apply the source apportionment results in support of the Georgia SIPs for PM and O_3 as well as approaches to improve regional haze, by providing information to guide emissions reduction efforts. Much of this work has been accomplished to date by VISTAS, and more recent work by EPA.[375] However, most RPO modeling has focused on long-term simulations (year-long) to date, using routine monitoring data (e.g., IMPROVE and STN) to evaluate performance, with the exception of Morris et al.[346,347] Thus, most modeling studies do not take advantage of the detailed chemical characterization and high-resolution data collected by the Supersites Program. Nonetheless, model performance evaluation results have provided the states and RPOs significant information about the performance of CTM and receptor-based models within their region.[336] For example, in the southeastern United States, CTMs appear to simulate sulfate dynamics reasonably well (within ~25%), likely because of the regional nature of sulfate (less variability in space and time as compared with primary species; e.g., EC and soil-related species), the better known description of sulfate formation within the models, and the more accurate measurements of both ambient sulfate and SO_2 emissions. Performance of the models for nitrate and especially SOA is poorer than for sulfate because formation mechanisms are not as well identified and classified in CTMs; the processes are often nonlinear; emissions estimates are not as well known; and ambient measurements, most often estimated for SOA by the EC tracer method as discussed earlier, have larger uncertainties than sulfate. Model performance of soil-related species and other primary species (e.g., EC) is less than for sulfate because there is considerable spatial variability as well as significant uncertainty in the emissions.[340,343,377] Uncertainties in meteorological modeling also contribute to the uncertainty of CTMs[378,379] and the lack of meteorological models to simulate hourly or better variations in meteorological variables likely limit the CTM's ability to simulate the fine temporal variations in PM mass and components.[380]

CTM modeling conducted by EPA using CMAQ and organic speciation data indicated that direct $PM_{2.5}$ emissions from motor vehicle exhaust were significantly overestimated in the Atlanta area.[348,375] This overestimation hides the fact that current models (e.g., CMAQ in this case) underestimate $PM_{2.5}$ SOA, and this uncertainty should be considered as SIPs are developed in Georgia.

Pittsburgh, PA; Baltimore, MD; and Mid-Atlantic Region. The mid-Atlantic has the advantage of two Supersites Projects within its region, one located in Pittsburgh, PA, and the other in Baltimore, MD. In addition, as part of the Mid-Atlantic Northeast Visibility Union (MANE-VU), the New York Supersites Project also supported this RPO. To date, most of the input has come from the Pittsburgh Supersites Project.[538] This information included methods evaluations and characterization of PM in the Pittsburgh region, which supported the development of a conceptual model for PM in the mid-Atlantic region.[381,538] Policy-relevant information, provided by the Pittsburgh Supersites Project, as listed in Table 13, is also beginning to be integrated within the MARAMA framework. A few key highlights that will likely influence emission management practices include the impact of SO_2 reduction on $PM_{2.5}$ concentrations and on the frequency of nucleation bursts that appear to occur on regional and local scales in western Pennsylvania. Characterization of the distribution of primary and secondary OC also are beginning to provide insights regarding reductions of OC and the impact of reducing primary OC emissions versus SOA precursors.[382]

As described earlier, regional and local nucleation bursts occurred on relatively clean, sunny days virtually anytime of the year on approximately 30% of the days (local and regional nucleation events occur on ~50% of the days) during the Pittsburgh Supersites Project measurements period.[279] UF PM reach much higher levels regionally than typically seen, even in urban Pittsburgh. These particles are initially acidic, thus also having potential health and environmental relevance. Measurements and modeling now indicate that the frequency of these events increases (more so in the summer than the winter) as SO_2 concentrations are reduced (i.e., as SO_2 controls go in place), whereas reductions in NH_3 concentrations appear to be effective at reducing their frequency, summer and winter.[291] In fact, the most recent modeling indicates that NH_3 is required for initiation of the nucleation bursts; that the initial particles are quickly neutralized; and when NH_3 is no longer available, the particles again become acidic because of growth by condensation of H_2SO_4.[283] Nucleation also ceases when NH_3 is no longer available.

Modeling of NH_3-HNO_3 or the NH_3-H_2SO_4-water system also provides insight into the influence of SO_2 reductions on $PM_{2.5}$ concentrations in western Pennsylvania.[349,350] Modeled predications using the Thermodynamic Model with Removal (TMR)[350] indicate that during the winter in Pittsburgh 50% emissions reductions in either SO_2, NH_3, or HNO_3 (i.e., reductions in NO_x) will lead to disproportionate reductions in $PM_{2.5}$ (8, 29, and 17%, respectively). These results and those of Takahama et al.[349] indicate that the area is often NH_3-limited. Therefore, reducing NH_3 will likely have the greatest benefits to reducing $PM_{2.5}$ in western Pennsylvania, but even more so if both NH_3 and SO_2 reductions occur simultaneously.

OC is composed of both primary emissions and secondary species, and each may be composed of hundreds or more compounds.[185] Thus, the development of effective control strategies will depend on understanding the contributions of both as well as the distribution of semivolatile organic species between the gas and condensed phase in both emissions and after atmospheric processing.[383] In Pittsburgh (July 2001–July 2002), annual average SOA accounted for 33% of particulate OC and for 30–40% of monthly average OC from June to November. This was similar to previous summertime estimates obtained during the 1999 Atlanta Supersites Project,[384] although larger estimates were observed in Los Angeles.[184] Results from Polidori et al.[382] suggest that multi-day formation and regional transport are important contributors to the higher SOA contributions to OC in Pittsburgh. Their results also suggest that SOA may be a particularly important contributor to OC in locations impacted by long distance transport such as the eastern United States.

CTM evaluations and initial applications continue to be performed in the eastern United States.[351,352] as well as comparisons to other modeling techniques (e.g., CMB). For example, as described in the emissions section above, Lane et al.[357] developed a source-resolved CTM and compared apportionment of primary OC and EC to results from CMB and to ambient STN and IMPROVE data collected in the eastern United States from July 12 to 19, 2001. The source-resolved model tracks particles from individual source categories or classes by splitting the emissions inventories into subcategories. The model is computationally efficient. Comparisons to CMB indicated significant problems with the emissions inventories as described earlier. However, RPOs have devoted significant efforts to improving emissions inventories but uncertainty remains. Russell[336] provides additional examples of comparisons among different CTMs and between CTMs and receptor approaches.

As SIPs in this region are developed, these results will continue to be integrated and finalized. However, simple approaches to emissions reductions may not be likely because of (1) differences in location and seasonal contributions to the various major components to $PM_{2.5}$ including primary versus secondary PM and components; (2) the significant influence of long-range transport to $PM_{2.5}$ levels, which also varies by season, location, and species; and (3) the still large uncertainties that exist in emissions inventories, measurements, and modeling.

St. Louis, MO, and Upper Midwest. The St. Louis Supersites Project was co-funded by the Midwest RPO, LADCO, and the State of Missouri to obtain data to support SIP development in the St. Louis, MO, area as well as the upper Midwest (Illinois, Indiana, Michigan, Ohio, and Wisconsin). This additional funding extended parts of the St. Louis Supersites Project into 2006. Therefore, results from the program are still in preparation. However, plans are underway to use the St. Louis Supersites Project data to support SIP development in Missouri and the upper Midwest through use of these data in CTM evaluation and application.[537,539] Currently, a few receptor modeling studies have been published for the St. Louis area and upper Midwest that included direct Supersites Project data.[326–328,332,385] Table 10 provides a summary of these results. On average for the sites examined in the Midwest, secondary sulfate is the most important individual source contributing to $PM_{2.5}$, whereas secondary nitrate was the next most important individual source. Sulfate mostly originated from the ORV and Tennessee River Valley, whereas nitrate was mostly of local origin, resulting from high NH_3 emissions in the midwestern region.[332] OM was spread over several sources on the basis of the use of organic species tracers in the CMB and PMF analyses, including all mobile sources (most important), burning (residential wood combustion and wildfires), industrial sources, and SOA. Several industrial sources were identified based on inclusion of trace elements as well, including, Zn and Cu smelting, Pb smelting, steel production, and Cu production.

Houston, TX, and Southeastern Texas. The Houston Supersites Project, also known as the Gulf Coast Aerosol Research and Characterization Program (GC-ARCH), was an integral part of the 2000 Texas Air Quality Study (TexAQS) (http://www.utexas.edu/research/ceer/texaqs/). Numerous researchers from the state agency (Texas Natural Resource Conservation Commission [TNRCC]), universities, federal agencies (NOAA, National Center for Atmospheric Research [NCAR], National Aeronautics and Space Administration [NASA], and EPA), and private industry contributed to the project along with GC-ARCH. The project has played an important role in understanding the formation and accumulation of PM and O_3 in southeast Texas. Results not only have influenced SIP development but also identified important areas of uncertainties that are being addressed through the TexAQS II (http://www.utexas.edu/research/ceer/texaqsII/index.html) conducted between May 2005 through September 2006 with a focus on regional air pollution rather than urban air pollution. Table 13 summarizes some of the SIP relevant findings resulting from the Houston Supersites Project.

A few specific results include the impact of biogenic VOC emissions on PM with formation of a significant amount of the SOA outside of Houston because of these emissions, whereas within the Houston urban area, anthropogenic emissions of aromatic species are the primary precursors to SOA formation.[212,241,386–390] Wildfires contributed significantly to primary $PM_{2.5}$ in Houston, on both an annual average basis and during specific air pollution episodes.[373] They can also contribute to secondary sulfate by catalyzing the oxidation of SO_2 to sulfate, leading to substantial additional sulfate formation.[373,391,392] Receptor modeling was applied to identify the sources of PM in the Houston area using OC marker species,[363,386,393,394] whereas photochemical CTMs were used to examine, for example, nitrate formation in relation to NH_3 sources, such as animal husbandry and industrial point sources.[395]

The Houston Supersites Project also had a major focus on O_3 formation and accumulation in the Houston area. Highly reactive hydrocarbons from industrial sources were identified as significant O_3 precursors, which led to new controls on these emissions sources.[396,397] Receptor modeling also was used to identify sources of high concentrations of VOCs.[398–400] Observational data and subsequent photochemical modeling revealed that anthropogenic chlorine emissions may play a significant role in urban O_3 formation in Houston[401,402] and a minor role in $PM_{2.5}$ formation,[403] although locally for short periods of time contributions to $PM_{2.5}$ may be significant (9 $\mu g/m^3$).

Fresno, CA, and Central California. The Fresno Supersites Project[6] has provided a wealth of information to serve several air quality related programs within California.[540] One of the most important was the Fresno Supersite's role as an integral component of the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS).[404] CRPAQS is a comprehensive $27 million program consisting of measurement methods evaluation, field monitoring in 1999 through 2001, emissions inventory development, data analysis, and air quality and meteorological modeling.

CRPAQS was designed to provide an improved understanding of the formation and accumulation of PM in Central California and to support development of effective control strategies for attaining the state of California and federal PM standards.

Results from the Fresno Supersites Project/CRPAQS have directly influenced SIP development within the SJV[405] and are being used extensively in the upcoming $PM_{2.5}$ SIP.[406,540] Uses include model performance evaluation and assessment of control strategies through application of air quality models. Much of the emphasis on measurements methods was associated with OC, EC, and NH_4NO_3, since during Central California episodes greater than 80% of the $PM_{2.5}$ mass is due to NH_4NO_3 and carbon. These episodes occur in the fall and winter and numerous exceedances of the $PM_{2.5}$ 24-hr NAAQS were recorded.[169,194] As mentioned earlier in this paper, the $PM_{2.5}$ FRM using Teflon filters can potentially be biased low relative to PM concentrations found in the ambient air because of volatilization of NH_4NO_3 and SVOC during collection, shipping, and storage. Results in Fresno also confirmed the loss of NH_4NO_3 from Teflon filters with average losses ranging from 8 to 16% of the $PM_{2.5}$ mass depending on the site and up to 45% for daily sampling.[32] Filter-based and continuous methods for OC and EC also were compared. Except for the R&P 5400, the methods appeared to be well correlated, but significant biases existed among the methods.[49,139,140] This result was expected, because the various measurement approaches are operationally defined and are likely measuring difference aspects of the carbonaceous aerosol.

An extensive network of monitors (three core sites and numerous supplemental sites) deployed throughout Central California for nearly 3 yr, allowed for a thorough spatial and temporal characterization of PM in various size ranges from south of Bakersfield up through Sacramento, San Francisco, and further north.[6] This campaign included measurements aboveground (up to 100 m) with a 100-m instrumented tower at one site (Angiola, CA, a rural site between Fresno and Bakersfield). Meteorological parameters also were measured at many sites throughout Central California. This extensive measurement program allowed for an improved understanding of the causes of PM accumulation within the SJV.[6,32,38,49,139,140,169,194,280–282,407–410] For example, in the winter, upper air transport (i.e., above the boundary layer) of accumulated $PM_{2.5}$ and precursor species is important for next-day impacts of secondary aerosols, particularly NH_4NO_3, resulting in regional impacts of NH_4NO_3.[194] OC, on the other hand, tends to have higher levels in the urban areas because of primary emissions from motor vehicles and residential wood burning, with the greatest impacts from motor vehicle emissions during the morning rush hour and from wood combustion in the evening. Both are trapped initially under a shallow surface layer, allowing significant concentrations to accumulate. These results were confirmed by spatial and temporal analyses of mass and related species and receptor-oriented modeling.[6,194,280,408,409]

Conceptual models for PM accumulation in Central California are described in Watson and Chow[194] and Turkiewicz et al.;[169] and the spatial and temporal characteristics of PM mass and chemical composition for several distinct episodes. These conceptual models update and augment that described by NARSTO.[165] Measurements from the Fresno Supersites Project also supported two exposure studies conducted within the Fresno area, the Fresno Asthmatic Children's Environment Study (FACES) and the Fresno Indoor/Outdoor Exposure Study.[411,412]

CONCLUSIONS

Policy-Relevant Insights

One objective of this synthesis is to interpret from the atmospheric sciences results policy-relevant insights of use to air quality managers and policy-makers who are developing emissions management strategies to meet air quality standards and designing networks to measure air pollution impacts. Results derived from the Supersites Program support the following policy-relevant insights.

Measurement Methods. Policy-relevant insights interpreted from the measurement methods results relate to uncertainties associated with current methods and suggest directions for future monitoring. A brief summary of measurement methods recommendations based on results from the Supersites Program has been provided by Solomon and Sioutas[413] and additional details are reported in Solomon and Sioutas[20] and Chow et al.[21]

- Results of the comparisons among measurement methods vary by location, season, operation (operator), and evaluation approach. As a result, scientists have developed various approaches to rectifying differences observed among the methods. Therefore, consistent standard operating procedures (SOPs) and calibration methods must be defined for each method.
- Integrated filter-based sampling methods can provide robust and accurate information if great care is taken to account for or eliminate artifacts associated with sampling, storage, and transport between the laboratory and sampling site and vice versa. These artifacts are often difficult to quantify, especially for OC collected on quartz-fiber filters. In addition, diurnal profile information important for understanding source impacts, acute health effects, and atmospheric processes is not obtained.
- Teflon filters (e.g., as used in the FRM) under a variety of conditions and especially during the summertime, underestimate actual ambient $PM_{2.5}$ mass concentrations by 10–40% because of loss of SVM from the filters. This loss is variable and unquantifiable without additional measurements. For example, a procedure based on the thermodynamic properties of particle composition, standard STN composition measurements, and available meteorological data have been developed to help reduce uncertainties associated with FRM volatility losses.[414] Additional validation is required to better understand how well this postprocessing procedure improves the $PM_{2.5}$ FRM mass estimates.
- Based on Supersites Program results, the FDMS-TEOM and D-TEOM (the latter is no longer commercially available) appear to provide the least

biased $PM_{2.5}$ mass concentration estimates, relative to $PM_{2.5}$ found in air, by minimizing sampling artifacts because of loss of semi-volatile species and water retention. Application of these or similar continuous methods will begin to allow for daily reporting of $PM_{2.5}$ data as well as a better understanding of the diurnal cycling of $PM_{2.5}$. These continuous instruments will fill important gaps in $PM_{2.5}$ measurements not previously obtainable in routine national networks operated on a 1-in-3- or 1-in-6-day sampling schedule. These more complete results will be significantly more useful for epidemiological studies by providing daily or hourly data to correlate with health effects endpoints.

- The current equilibration process for filters at 35 ± 5% RH is unlikely to remove all of the water associated with $PM_{2.5}$ samples collected during the summer months when particles are likely to be acidic. Neutral wintertime results indicate particles are essentially dry below 60% RH.
- Many of the continuous species-specific methods for PM composition still require evaluation and improvement before application in long-term routine monitoring networks. However, calibration of continuous methods data (e.g., 1-hr average data) to 24-hr filter-based data appears to provide comparable daily data that allow hourly results to be used with higher confidence. This quality assurance step requires a continued dependence on 24-hr average filter data, likely collected on fewer days than currently collected. This approach supports an earlier recommendation by the Clean Air Scientific Advisory Committee (CASAC).[415] Although this recommendation by CASAC was for $PM_{2.5}$ mass, this finding suggests it also may be applicable to use the filter-based daily average data to calibrate the continuous chemical speciation methods to be deployed in future networks.
- Continuous methods to directly measure PM_c are showing promise and have been under consideration by EPA as FEMs for PM_c. These currently include the PM_c TEOM and PM_c beta attenuation monitor (coarse particles measured using a BAM detector). A continuous $PM_c/PM_{2.5}$ dichotomous FDMS-TEOM is available commercially from Thermo Fisher Scientific, Inc.
- The continued development of sampling and analytical methods to identify and quantify polar organic compounds and oligomeric compounds and their precursor monomers is important because these species probably compose a significant fraction of the unidentified OC, especially the SOA fraction.
- A method for detecting unrecognized sources and determining emissions of toxic substances from individual stationary sources using highly time-resolved data provided by SEAS-II and PDRM has been described. SEAS-II has been shown to provide valuable highly time-resolved elemental data for source apportionment and temporal exposure patterns for elements and endotoxins in ambient air.
- Single-particle mass spectrometers and AMS provide a wealth of information on the chemistry and size of particles that are allowing for new insights into atmospheric chemistry and source-receptor relationships. It is safe to say that particle mass spectrometers represent the single greatest advancement in PM measurements methods technology in the past decade.[20]
- Size distribution measurements and particle number concentration measurements are now being obtained routinely in research studies from 3 nm to 10 μm. Their application is allowing new insights into our understanding of nucleation and growth of UF PM to the accumulation mode. They also provide input data to source apportionment models. Application in routine monitoring networks (e.g., EPA's new continuous monitoring network referred to as NCORE)[416] should be considered.
- Important fundamental parameters such as particle density are beginning to be measured more routinely using, for example, the differential mobility analyzer (DMA)-aerosol particle mass analyzer (APM). Although this method still requires evaluation, the need to have reliable density measurements is important for converting between size distribution and particle number concentration data to mass concentration.
- DAASS has emerged as a method to directly measure PBW in PM_{10} or $PM_{2.5}$. Although additional testing is required, application of this method has allowed the mass balance to be closed within measurement error on an hourly basis and for an entire year. Results indicate that in the Pittsburgh area, PBW is tied to acidity and because the aerosol is often acidic in the summer, particles also have a much higher water content in the summer than the winter.

Characterization. Characterization of PM describes variations in space and time of the full spectrum of PM, including mass in various size ranges, the chemical components of PM, precursor species, and other related pollutants. Secondary components are discussed in Fine et al.[186] and spatial and temporal variations are described in Turner and Allen,[417] Allen and Turner,[418] and Demerjian and Mohnen.[166]

- Annual average $PM_{2.5}$ mass concentrations exceeded the $PM_{2.5}$ annual average NAAQS value at all of the Supersites Project locations except Houston. Daily values only exceeded the $PM_{2.5}$ 24-hr NAAQS value in Fresno, although Baltimore reported a single exceedance in July 2002 as the result of the transport of smoke from the Canadian wildfires. These results reflect the establishment of the annual standard as the controlling standard by EPA with its 1997 PM NAAQS. However, both peak and long-term average concentrations may need to be lowered to meet the

new 2006 $PM_{2.5}$ 24-hr NAAQS requirements, because all locations reported daily average values greater than 35 $\mu g/m^3$ (see Table 7b).

- Results from the Supersites Program continue to reaffirm that the relationship of the major components of PM has not changed much during the last decade, with sulfate and OC typically the highest in the eastern United States, whereas nitrate and OC are the most abundant species in the western United States. In the East, ammonium, nitrate, EC, and crustal-related elements compose the bulk of the remainder of ambient PM. In the West, ammonium, sulfate, crustal-related elements, and EC compose the bulk of the remainder of ambient PM. These results suggest different control strategies might be appropriate for different parts of the country.
- In the eastern United States, $PM_{2.5}$ mass has a strong regional component often driven by the regional nature of sulfate and secondary OC, although local sources of carbon (OC and EC) and other primary species also are important contributors to $PM_{2.5}$ in urban areas. As such, urban concentrations are superimposed on regional levels, so urban areas typically have higher concentrations than rural areas. In Fresno during the winter, nitrate is regional whereas OC and EC are higher in the urban areas because of primary emissions where motor vehicles dominate in the morning and residential wood burning in the evening. The regional nature of nitrate in the SJV is at least partly driven by transport of nitrate and nitrate precursors aloft during the night with downmixing the next morning.
- Seasonal variations in PM are often driven by changes in secondary components, with sulfate and SOA more dominant in the eastern United States during the summer and nitrate more important in the winter, especially in the western United States. In Houston, sulfate is slightly higher in the spring and fall, whereas carbon is highest in the late fall. In the eastern United States during the summer, SOA approaches up to 40% of the OC on average, whereas during O_3 episodes up to 80% of the OC appears to be secondary. Primary particles appear to be more dominant in the winter because of lower mixing heights and reduced photochemistry required to produce the oxidants for sulfate and SOA formation, although photochemistry still takes place with measurable free radical concentrations.
- Aerosol composition is different in different particle size modes (UF PM, accumulation, and PM_c) and the composition within these modes varies considerably spatially and temporally, including between source and receptor sites within the same air basin and on time scales ranging from minutes to days as well as by season. These differences reflect the impact of different and variable sources, atmospheric chemical processing, transport, and meteorological conditions, both on local and regional scales.

These results and those in the previous two bullets suggest that different control strategies may be needed depending on location and time of the year (i.e., regional and seasonal controls) for some PM components or their precursors to cost effectively reduce ambient PM concentrations to below current PM air quality standards. However, consideration of other non-PM-specific pollutants, such as O_3, need to be considered in this analysis, because it is possible to reduce an O_3 precursor to reduce PM, yet increase O_3 concentrations, either near the source or downwind (see for example, Schere and Hidy,[419] and NRC[420]). The importance of these tradeoffs needs to be examined on a case-by-case basis. Similarly, reductions in a direct PM precursor such as SO_2 can result in an increase in another PM component, such as nitrate, because reductions in SO_2 yield reductions in sulfate (in $PM_{2.5}$ as $(NH_4)_2SO_4$), but then the associated NH_3 is available to react with HNO_3 forming particulate nitrate in the form of NH_4NO_3.

- On the basis of ^{14}C measurements in urban and rural areas, biogenic sources appear to be major contributors to $PM_{2.5}$ OC, even in major urban areas such as Los Angeles, CA. These sources may be anthropogenic (e.g., residential wood burning or charbroiling) or natural (e.g., forest fires ignited by lightning).
- SOA formed from biogenic VOC precursor species can be an important contributor to total SOA. For example, north of Houston most of the SOA appears to be from biogenic precursors formed as oxidants created in the Houston urban area are transported and mixed with air masses rich in biogenic VOC species emitted to the north of the urban core. However, close to the urban and industrial areas of Houston, aromatic VOC species are significant SOA precursors. These results suggest that ambient concentrations of O_3 and other oxidants within the greater Houston area may need to be reduced to decrease levels of SOA both in urban and rural areas of southeastern Texas.
- Driven by thermodynamics, nitrate has the largest consistent diurnal variation, with higher concentrations observed under cooler, more humid conditions, such as those experienced in the early morning. This variation was observed in summer and winter at all locations although in most locations, most of the nitrate was found in the particle phase in the winter. This result suggests that sufficient HNO_3 is available year-round and that under these conditions the atmosphere is likely NH_3-limited, thus providing an avenue for sulfate replacement as SO_2 reductions are implemented to lower sulfate concentrations.
- Carbon is usually the major component of the smallest UF PM under most urban conditions, although $(NH_4)_2SO_4$ also can be a major component during regional nucleation bursts that occur frequently in the eastern United States and during periods when an SO_2 plume (e.g., from a

coal-fired power plant) directly impacts the monitoring site (e.g., Atlanta, GA, and Rochester, NY). The smallest particles are often externally mixed. Near industrial sources, such as in Houston, UF PM may be mainly composed of trace elements and their oxides, although carbon is usually present as well. The smallest UF particles often grow to larger UF PM sizes and to the accumulation mode by condensation of secondary components such as sulfate, nitrate, and SOA; these particles are internally mixed. Particles mass spectrometers have provided considerable insight into these processes.

- In Los Angeles, studies of UF PM near roadways indicate that UF PM particle number concentrations drop rapidly from the roadway near the source to much lower values just a few hundred meters downwind. UF PM particle composition also changes because of the balancing effects of condensation and evaporation as particles move from near the tailpipe to a few to tens of meters away from the tailpipe and are diluted with ambient air.
- In the eastern United States (Pittsburgh), PBW was found to account for a significant fraction of the aerosol mass, especially in the summer (~15%; 8% on average in the winter) with the highest water content observed when the aerosol was acidic (up to 50% of the sulfate was in the form of NH_4HSO_4). In the summer, appreciable PBW is associated with $PM_{2.5}$ below 30% RH, whereas in the winter particles are essentially dry below 60% RH. These results suggest that PBW should be measured routinely to reduce uncertainty in source apportionment results. They also suggest that the current FRM filter equilibration process at 35% RH is unlikely to fully remove PBW from samples collected during the summer.
- Meteorology drives transport and the duration of pollution episodes. In most locations, the highest pollution episodes occur during multi-day periods of stagnation often impacted by regional transport and recirculation with clearing because of washout and/or passage of a frontal system or other meteorological event.

Estimating Source Contributions. Source contributions at receptor sites are estimated by both receptor-oriented (starting at the receptor and working back to the source; Watson et al.[303]) and source-oriented approaches (starting at the source and working forward in time to the receptor; Russell[336]).

- Understanding source-receptor relationships, especially in the eastern United States, is complicated because urban PM concentrations are superimposed on significant regional PM levels. The regional impact may be from upwind urban or rural areas and be from both natural (including biogenic) and anthropogenic sources with a considerable secondary aerosol component. Use of receptor models has helped to quantify the impact of transported secondary species, indicating that up to 90% of the aerosol in Pittsburgh and 50–90% in NYC are transported from upwind areas during the summer. In the winter, local emissions are more important.
- Use of continuous species-specific methods with newly developed mathematical receptor-oriented approaches, including results from particle mass spectrometers, size distribution measurements, and VOC data, provide an unprecedented ability to identify the contribution from primary sources to observed ambient concentrations, particularly if long-term databases are developed to support future PM SIPs.
- Fifteen receptor-oriented models were applied as part of the Supersites Program, each with different advantages and disadvantages. The availability of the continuous PM data (i.e., mass, composition, and/or physical properties), along with meteorological variables (e.g., WD and back-trajectory analysis) also available at high-time resolution, allowed the application of receptor models to move from identifying source types to identifying specific sources and their contribution to ambient concentrations.
- Additional work is needed to identify sources of the precursor species to SOA. This work needs to include identification of the precursor species that form polar organic compounds and quantify oligomers that may comprise a significant fraction of the SOA or OC mass.
- A hybrid model (PDRM), taking advantage of the continuous data with a receptor model in conjunction with a Gaussian model and other variables, including knowing the location of possible sources, allowed for estimates of not only specific source contributions at the receptor site but also source emissions rates. These estimates were within 10% of independently obtained emissions estimates for the species of interest. This model likely represents one of the most significant advances in source apportionment modeling tools resulting from the Supersites Program.
- The utility of source apportionment using receptor models depends on the model inputs available and the model used. For example, apportionment of secondary sulfate, nitrate, ammonium, and OC will not be obtained if only trace elements are used in the analysis. Thus, the most complete apportionment requires measurement of as complete a set of chemical components as possible, including organic compounds that have previously been identified as important markers for specific sources (e.g., see Table 9, a and b). To date, advanced ambient data collection (including meteorological parameters) has allowed for the identification of up to a dozen source types and/or specific sources. However, these include secondary components (sulfate, nitrate, ammonium, and SOA) that most often cannot be directly tied back to specific source types or sources if only receptor models are used.

- Recent findings indicate that some organic species used in receptor modeling (i.e., CMB) as tracers or markers for specific source types may not be stable in ambient air as a result of photochemical oxidation or other processes that influence the concentration of these species on time scales associated with regional air masses (days to weeks).
- Considerable variability among published source profiles for a given source type have been noted when comparing organic marker or tracer species and ratios of species. This variability in source profiles, along with the influence of aging and choice of marker species, can result in significant uncertainty in source apportionment estimates developed by CMB (e.g., factors of 2–10 and greater have been reported) and this has important implications if only CMB were used for the development of SIPs. Other factor analysis methods, such as PMF and UNMIX that develop source profiles as part of their analysis, will not be impacted as significantly by this issue.
- Receptor modeling efforts by the Supersites Program and related studies using back-trajectory analysis reaffirms and quantifies that transport of SO_2 and its reaction product, sulfate, from the upper Ohio River Valley, impacts New York, Pittsburgh, and St. Louis as well as other parts of the upper Midwest. In Pittsburgh and St. Louis (and the Great Lakes Region), this transport appears to occur on the backside of high-pressure systems as the high moves eastward from the upper Midwest to the Northeast.
- Motor vehicle emissions are major contributors to UF PM and $PM_{2.5}$ OC, with the greatest influence in the morning during rush hour and when inversion levels are still relatively low. Photochemical processes contribute significantly to afternoon peaks in sulfate and SOA, whereas residential wood combustion tends to have its greatest impact on OC in $PM_{2.5}$ in the evening and early nighttime.
- Forest fires in the eastern and western United States, including long-range transport from outside the United States, can lead to high $PM_{2.5}$ levels over large geographical areas as reaffirmed by Supersites Program and related studies measurements. For example, long-range transport from 1000 km or more was identified in Baltimore during the first week of July 2002, when transport of smoke from Canadian wildfires impacted the Baltimore Supersite, resulting in their only exceedance of the 24-hr $PM_{2.5}$ standard during the study period.
- Intercontinental transport of dust from North Africa and Asia has been identified as a source of PM in the United States. For example, a large Saharan dust episode impacted PM levels across the eastern United States in early July 2002. This episode significantly influenced $PM_{2.5}$ concentrations in St. Louis before moving eastward. Major natural events (forest fires and dust events) cannot be controlled and their impact on $PM_{2.5}$ levels may need to be considered in areas close to attainment.
- Evaluation and application of CTMs using Supersites Program data is just beginning because of the extensive inputs required to operate these models (see Russell[336]). Most testing of the full CTM has been done outside the Supersites Program (by RPOs and EPA), because application of CTMs was not one of the objectives of the program. However, the high-time resolution species data are helping to revise the conceptual models of PM formation and accumulation and identify the need for model improvements.
- Continuous methods are providing unique data for evaluation of TEMs/modules. TEMs are already showing promise for use in estimating impact of SO_2, NO_x, and NH_3 controls on sulfate, nitrate, ammonium, and regional nucleation bursts observed in the eastern United States.
- Both receptor-oriented and source-oriented approaches have limitations, but they complement each other so use of both are advised to obtain the best estimates of the impact of sources or source types at receptor locations.

Emissions: Estimates, Inventories, and Uncertainties. An accurate understanding of source emissions is required to develop effective control strategies to reduce PM levels in air to below NAAQS. Emissions estimates and inventories are fundamental inputs to CTMs, provide clues to the most important sources within an area, and allow for tracking trends as controls are implemented and/or as source activity changes over time. Developing emissions estimates and inventories was not a primary goal of the Supersites Program, but efforts were conducted to support the other objectives. Simon et al.[338] examined uncertainty in emissions inventory estimates comparing bottom-up (measuring emissions directly) and top-down (on the basis of modeling and field observations) emissions estimates. Direct and indirect source emissions measurements were also obtained.

- A factor of 2 or more in uncertainty in PM emissions estimates was observed in the source categories examined by Simon et al.[338] Similar uncertainties exist for emissions estimates of precursors of secondary species, with the exception of pollutants monitored by continuous emissions monitoring (e.g., SO_2 from major point sources).
- Emissions estimates conducted through the Supersites Program provided improved emissions estimates for several source types or sources (e.g., coke plant), allowed for different control strategies to be evaluated (e.g., diesel busses), and provided new indirect methods for estimating source emissions (e.g., application of PDRM).

Control Strategy Relationships of Secondary PM and O_3 to Precursors. PM is a complex atmospheric pollutant and control strategies to reduce one pollutant (e.g., sulfate) may inadvertently increase another (e.g., nitrate). However, as with model applications, the effect of emissions controls on both PM mass, PM components, and other

pollutants are just emerging. However, several conclusions have been suggested based on application of TEMs and CTMs, and they are summarized here.

- TEM are beginning to be used to understand the sulfate-NH_3-HNO_3 system with most efforts occurring in Pittsburgh and the southeastern United States, although extension to other parts of the East Coast may be possible.
- In the eastern United States, NH_3 often appears to be the limiting reagent in the formation of nitrate, at least during the winter. Results from St. Louis also suggested the importance of agricultural sources of NH_3 to particulate NH_4NO_3 concentrations. Therefore, significant substitution of sulfate by nitrate is predicted for the winter months in Pittsburgh if SO_2 emissions are reduced (NH_3 not reacted with H_2SO_4 is now available to react with HNO_3) with lower reductions in $PM_{2.5}$ than would be predicted otherwise. Results suggest this increase in nitrate can be prevented by reductions in NO_x or NH_3 emissions. However, NH_3 reductions seem to provide the largest benefit for lowering PM concentrations, although reducing NH_3 could raise the acidity of the atmospheric aerosol. Substitution of nitrate for sulfate is predicted to be small during the summer months for the same area.
- Regional nucleation bursts observed in the Pittsburgh area and elsewhere are because of the H_2SO_4-NH_3-water ternary system. TEM results indicate that 50% reductions in SO_2 will increase the frequency of these events during the summer and reduce the frequency in the winter. Controls of NH_3 emissions are predicted to decrease the frequency of these events during both the summer and winter. A combination of SO_2 and NH_3 emission controls can decrease the frequency of nucleation events and $PM_{2.5}$ concentrations without increasing atmospheric acidity.
- Measurements of the total available (gas and aerosol) NH_3 and total HNO_3 are important both for the evaluation of the available modeling tools and for use as input to observation-based models that can be used for the design of emission control strategies. These variables should be measured in routine networks.
- Initial CMAQ modeling in Atlanta using Supersites Program data examined the effect of various controls (NO_x, VOC, SO_2, NH_3) on $PM_{2.5}$ mass and O_3. These first-order tests (100% control) begin to provide direction and magnitude on the effects of controls on multiple pollutants, such as $PM_{2.5}$ and O_3.
- Although considerable progress has been made in the last 5–10 yr with regards to PM measurements and modeling, considerable work is still needed, including further advancement (development and evaluation) of continuous species and physical property specific methods for use in routine monitoring networks and integrated and/or continuous methods for organic speciation on a more routine basis. Developing improved emissions inventories for OC, EC, mobile/area NOx, VOC, and NH_3 are needed as well as obtaining accurate meteorological fields on an hourly or better time frame, both needed to drive the emissions based air quality models. Considerable efforts are needed to ensure the models are correctly simulating SOA and the partitioning of sulfate, nitrate, and ammonium between the gas and condensed phases. More work is needed to ensure models are correctly apportioning primary versus secondary and anthropogenic versus biogenic fractions of OC and inorganic components. Nucleation is not well simulated in the models, and there may be a lack of scientific foundation in the models to address this recently identified issue.

Health-Relevant Insights

As atmospheric science findings can be interpreted in terms of policy-relevant insights, so can they be interpreted in terms of their relevance to the health and exposure communities. The advances made through the Supersites Program in characterizing and understanding the fate of PM from source to receptor and linking receptor concentrations back to source emissions provide a basis for focused future research in the areas of PM-related health effects, exposure, and toxicology. Specifically, coupling PM measurements with health and toxicological studies aimed at identifying the toxic properties of various components to which people are exposed provides insights for identifying health endpoints associated with PM exposure.[3,421–423] These results then provide a basis for identification and targeted control of the specific types of PM that pose the greatest risk to public health. The key achievements from the Supersites Program that can be linked to and support health effects, exposure, and toxicological research include:

- Unique particle composition data supplied by single-particle mass spectrometers can be used in conjunction with receptor modeling to determine the sources of the UF PM particles to which people are exposed through ambient air. Significant differences are reported in UF PM composition measured by single-particle mass spectrometers in four cities (Baltimore, MD; Pittsburgh, PA; Atlanta, GA; and Houston, TX). Although OC was observed in a significant fraction of particles in all locations, differences in the relative number of particles containing sulfate, nitrate, and trace metals, including potentially toxic species (e.g., Pb, Zn), varied among the cities and by season. The nature of organic species likely varies according to source, atmospheric chemistry, and meteorology. Further characterization of the organic content in relation to these variables is necessary because metal and organic content appear to be particularly important in the health effects associated with PM exposure.[424–426]
- Compositional attributes of UF particles may be more important than either mass or particle number concentration. The bioavailability of PM components may vary according to size. Toxicological studies are needed to identify which

sources or compositional characteristics of UF PM particles are associated with the greatest toxicity, so that effective controls can be developed to reduce exposure to the most toxic particles. These issues may be investigated more successfully in the future using particle MS and other measurements data (e.g., continuous measurements) in association with toxicologically studies.

- Supersites Program data indicate UF PM mass, UF PM particle number concentration, and $PM_{2.5}$ mass are generally poorly correlated with one another. $PM_{2.5}$ cannot be used as a surrogate for UF PM mass or UF PM number concentration. Similarly, UF PM number is not a surrogate for UF PM mass. These findings are important because EPA-funded PM Health Effects Research Centers (Particle Centers)[421] have determined that UF particles possess several toxicologically important properties. These properties include chemical reactivity, the ability to produce oxidative stress in a variety of experimental systems,[426] and the ability to translocate from the site of lung deposition to other tissues via systemic circulation.[427] It is not yet clear whether UF PM particle number, surface area, mass, or chemical composition is the most highly relevant metric, the latter noted in the previous bullet. Additional combined PM measurement, toxicological, and health-effects studies of these variables are needed to determine the appropriate components that cause the highest risk.
- Little UF PM data (size distribution or even just particle number concentrations) are currently being collected within the United States. It is suggested that additional long-term studies begin to include these and related variables so an adequate assessment of the health-effects from UF PM can be obtained. The methods to make these measurements (e.g., CPC, SMPS) are commercially available, evaluated, and widely used in short-term research studies.
- Extensive development and application of continuous sampling methods in the Supersites Program has produced data on the concentration of PM at a variety of locations over time scales ranging from less than 1 min to seasonal averages. This allows for uninterrupted daily data as well as measurements of transient high concentrations so that exposure studies can examine potential health impacts of variability in exposure to PM-related pollutants on hourly or shorter time periods. These source-driven transients are superimposed on daily and seasonal profiles that are driven by synoptic meteorology that controls transport distance, ventilation, and photochemistry. Exposure measures that are averaged over longer time intervals have applications in exposure assessment for chronic health effects including atherosclerosis.[428] In contrast, there are many mechanistic and health endpoints that are likely to be associated with exposure peaks and short-term transients. An important recent example of the latter is the finding that time spent in traffic was associated with an almost 3-fold increased risk of a myocardial infarction 1 hr later.[422] Continuous PM measurement methods provide a database that allows epidemiologists to rigorously ask which exposure parameters and averaging times are most relevant for exposure response analysis of a particular outcome of interest.
- Ambient concentrations of PM are often too low for effective laboratory experiments with a limited number of animal or human study subjects. Results from the Supersites Program indicate that particle concentrator technologies, such as the Versatile Aerosol Concentration Enticement System (VACES) developed by the Southern California Particle Center and Supersite, introduce negligible to slight artifacts to the mass and compositional distribution of ambient aerosols, and can provide concentrated UF PM, accumulation, and PM_c particles for a variety of studies. The need for concentrated particles is especially important for studies of UF PM particles, which represent a small fraction of total ambient $PM_{2.5}$ mass, but have been shown to possess important toxicological properties.[426,427] Increasing the concentration of particles per unit volume is important for experimental exposure studies because it enables more powerful study designs and performance of controlled dose-response studies, which may play an important role in future standard setting. Concentrated PM collected by VACES also has important uses for chemical and in vitro studies designed to elucidate the mechanisms by which PM exposure produces associated health effects. For example, sample collection by the VACES system was instrumental in the identification of UF PM as possessing the greatest oxidation-reduction activity and induction of protective enzymes, thereby providing insights on the mechanistic features of PM toxicity in studies conducted in Southern California.[426]
- The loss of semi-volatile components from Teflon filters, as noted previously, results in an underestimation of total mass, and if these filter samples are used in toxicological assays the potential health effects of semi-volatile compounds will be missed. Methods evaluated in the Supersite Program that account for or reduce the loss of semi-volatile PM components (e.g., FDMS) should be applied in future health, exposure, and toxicological studies. Studies designed specifically to assess the toxicological properties of the semi-volatile components of PM are needed. For example, studies to determine the potential of PM to induce oxidative stress have demonstrated semi-volatile components as possessing the greatest potential health effect.[429]
- Although PM concentration and composition vary on short time scales because of the impact of sources and meteorology, Supersites Program research found that the relative abundance of the

major PM components (sulfate, nitrate, ammonium, OC, EC, and crustal material) are, on average (e.g., seasonal and yearly), relatively consistent across many locations and within major regional areas (e.g., eastern United States, eastern Texas, Central and Southern California). The level of consistency in PM observed may explain why daily acute mortality and PM mass concentrations show temporal associations in time-series studies of large cohorts,[430,431] although the specific size distribution and chemical composition of PM differs in different urban environments. Measures of exposure to specific PM components or characteristics may provide a more robust set of data to allow statistical analyses to detect specific health effects.

- The contribution of SOA to carbonaceous PM is quite variable over 1 to several days in the eastern United States and is positively correlated with increased O_3 concentrations, raising the question of possible chemical interactions between SOA and O_3 on health endpoints.
- Characterization of particle-bound organic compounds was a vital element of the Supersite Program. Organic compounds are components of fuels, produced by combustion processes, emitted by natural sources (e.g., vegetation), and are formed in air via atmospheric reactions (SOA). The composition of organic compounds may vary based on source, location, season, time of day, and chemistry across geographical areas. For example, a hydrocarbon may be oxidized to carbonyls as a first stage and later to carboxylic acids; the toxicity, therefore, may vary with time and space. Secondary OC appears to be composed largely of polar organic and oligomeric compounds. Many of these are likely more water-soluble and to some extent with unknown potential toxicity; thus dose may be enhanced by their solubility in the aqueous lung lining fluid relative to the reduced forms of these compounds. Research conducted in the Particle Centers has shown that oxidative properties of PM may be an especially important element of toxicological mechanisms.[426,432,433] Identification of PM-associated carboxylic acids, OH- and carbonyl-containing compounds, and other water-soluble organic components suggests hypotheses for further research to define the toxicological properties of these compounds and the need for their continued identification and quantification in PM. The characterization of species, such as carbonyls, which are capable of electrophilic chemistry, and quinones, which generate ROS catalytically as well as participating in electrophilic chemistry, is particularly important. It is possible that the oligomeric compounds also possess oxygen moieties that are capable of ROS generation.
- Concentrations of UF PM particles increase dramatically on clean days in the eastern United States over regional areas extending at least to hundreds of kilometers because of homogeneous nucleation. These nucleation bursts likely begin as H_2SO_4 aerosols that are quickly (within 1 hr), in part, neutralized by NH_3. The composition of these particles is dramatically different from the composition of the fresh UF PM particles emitted by transportation and other combustion sources, which are largely organic in nature. Therefore, if the composition of UF PM particles affects their potential health effects, one might expect spatial differences across cities or regions on the basis of the mechanism of formation of the UF PM particles. However, because regional nucleation bursts occur on clean days the health effects may not be observed until several days later when people may be exposed to higher concentrations of PM, after first being sensitized by the UF PM in the nucleation bursts a few days earlier.
- The size distribution, composition, and concentration of UF PM particles formed at a freeway were found to be significantly different from the size distribution, composition, and concentration of those same particles a few hundred meters downwind of the freeway because of condensation, evaporation, and dilution.[273–276] Therefore, exposures and associated health effects of UF PM particles near the roadway and during commuting may be significantly different compared with just a short distance away. For example, PAHs are found primarily in the UF PM mode near vehicular emission sources and in the accumulation mode downwind of source emissions. During spring and summer, at downwind receptor sites such as Claremont, CA, a significant fraction of PAH species also reside in PM_c.[77,434]
- Development of the DAASS[117] at the Pittsburgh Supersite allowed water associated with ambient aerosols to be estimated with sufficient accuracy to allow for near closure of PM mass by chemical components. The water content of aerosols appears to increase as particle acidity increases, especially in the eastern United States under high pollution episodes during the summer. These particles are not only acidic, but may contain higher concentrations of potentially toxic trace metals and water-soluble organic species in the liquid phase, allowing quicker transfer from the particle to lung fluids, with potential enhanced adverse health effects under these conditions.
- Seasonal differences in $PM_{2.5}$ are mostly the result of variations in secondary aerosols (inorganic and organic). These findings suggest the need for toxicological characterization over multiple seasons to further clarify the role of secondary aerosols in overall PM toxicity. Oxidation of compounds, such as PAHs in summer, may result in secondary aerosol of greater toxicity.[435]
- The size distribution data collected in Southern California during the wildfires of October 2003 indicated that the aerosol produced by these fires was larger than typical urban aerosols and penetrated more efficiently into houses. Public health

directives for periods of wildfires, such as warnings to stay inside to avoid fire-related pollution, should consider the impact of penetration of particles into houses because people were told to stay indoors to protect themselves from the higher PM levels, yet that may not have been sufficient to avoid adverse health impacts from these fires, especially for sensitive populations.

- The simultaneous mix of NO_x and reactive organic precursor species from primary industrial emissions appears to result in high concentrations of carbonyl and organic nitrates, unique to Houston, TX. The potential health effects of these species should be considered in future toxicological and health studies in Houston.
- Nearly parallel to the years of the Supersite Program, EPA developed a major program to address critical research gaps in exposure, dosimetry, toxicology, and epidemiology of PM, as outlined by NRC.[361] The Particle Centers have generated substantial and important data on toxic mechanisms, clinical findings, and epidemiological studies. Additional efforts should be made to evaluate and integrate the combined datasets and findings to allow for better integration among these important and often-viewed disparate disciplines.

KNOWLEDGE GAPS

Measurement Methods

Many uncertainties still exist in the measurement of PM, whether filter-based or continuous:

- Continued efforts are needed to determine analytical characteristics (e.g., precision, bias, accuracy, interferences) for continuous methods to ensure that uncertainties are quantified among methods and between the measured values and what is actually present in the ambient air.
- Development of reference standards is critical to help understand sampling artifacts and to obtain accuracy information (method bias relative to a reference standard) about methods that includes both sampling and analytical uncertainties. In particular, standards are needed for OC and EC measurements because differences between analytical methods can be as much as 20% for OC and 200% or more for EC. Producing reference standards for PM is a complex issue and few efforts are occurring to develop them.
- Methods for near-real-time measurements of trace elements are lacking, specifically those useful for source apportionment and trace metals potentially responsible for adverse health effects. High-time resolution data (30-min samples) are obtained with sample collection (e.g., using the SEAS) and subsequent analysis in the laboratory, although long time delays can occur between sample collection and reported results because of the nature of this process. Efforts also are underway to develop a field-deployable XRF system with an upfront aerodynamic lens to concentrate the particles into a small spot.
- Continued efforts are needed to quantify single-particle methods and to better understand uncertainties associated with measurement of single particles versus the more widely used bulk methods, integrated or continuous.
- Considerable progress has been made in the measurement of polar organic species, oligomers, and polymers in ambient PM. However, even with these new efforts, only a maximum of approximately 50% or so of the OM has been identified, and a major fraction of that portion is only identified as, for example, HULIS or oligomeric, and not as individual species. Efforts to continue methods development in this area are critical to further our understandings of the formation and fate of OC in the atmosphere.
- Development of continuous methods for organic species or classes of species are needed; recent work using particle mass spectrometers and thermal desorption GC-MS[152] is beginning to move forward along these lines.
- Significant differences still exist between the various methods to measure OC and EC (and BC) because of differences in the analytical protocols and methods for blank-correcting OC. Because these methods, to date, are operationally defined, agreement is needed to harmonize the protocols or to develop SRMs that can quantify the uncertainty in the methods.
- Comparability of various methods designed to measure similar PM parameters and used in different regions of the country or across networks is lacking. This is important because we now realize the extensive regional nature of PM. If differences exist, algorithms should be developed to make the data more consistent and additional methods comparisons should be implemented to determine why there are differences and then develop methods with the least bias and lowest uncertainty.

Characterization

- Continued efforts are needed to characterize the physical and chemical attributes of UF PM, its formation, and its growth to larger sizes.
- Chemical characterization of PM_c in multiple locations is needed, given the differences and similarities observed in PM_c concentrations across various locations (e.g., during the multilocation evaluation of the continuous PM_c samplers as potential FRM or FEM).[100]
- The vertical distribution of PM and PM precursors and the transport of these species aloft is still a mystery in most locations. This is important because transport of precursors and PM, especially secondary aerosols, over long distances impacts PM levels in most regions of the United States. Transcontinental transport from Asia and Africa is also important at times. These uncertainties require measurements of air pollutants aloft and

suggest a greater need for the integration of remote sensing methods from the surface (e.g., LIDAR) or from space using satellites.

- A large fraction of OM is still not identified or classified. Much of this portion of the aerosol is believed to be oxygenated organic compounds, but measurement of oligomers and larger polymers also is required.
- Improved methods to estimate SOA are needed, especially because SOA can contribute significantly to OC concentrations on urban and rural scales. Use of daily average concentrations of OC and EC can lead to an underestimation of SOA by the EC tracer method, relative to the use of continuous methods, when similar analysis methods are used between the filter and continuous methods (e.g., both use similar thermal protocol and pyrolysis correction approaches).
- The role of acidic seed particles in enhancing SOA formation is currently uncertain with chamber studies and 24-hr measurement data suggesting its potential importance but field studies using hourly data suggesting that it may not be important in the atmosphere. A better understanding of the mechanisms by which SOA is formed and the role of acidic aerosols is needed to reduce uncertainty in SOA modeling and impacts on SOA because of reduction of emissions, especially reductions in SO_2 and NO_x, which are acidic particle precursor species.
- More work is needed to distinguish anthropogenic versus biogenic components of PM, especially for SOA, because significant fractions of SOA may be due to emissions of natural biogenic precursors. The effect of the control of oxidant levels on the formation of SOA needs further clarification.
- Improved characterization of the linkages among pollutants (e.g., PM, O_3, NO_x) is needed to develop the most overall cost-effective and efficient emissions control strategies for ambient pollutants.

Receptor- and Source-Oriented Models and Modeling

- A variety of receptor models have been developed and tested as part of the Supersites Program. Differences exist among the sources and estimated source contributions identified and quantified by the models. Efforts should continue to refine these models and/or needed ambient and source measurements to allow for results that are more consistent.
- Numerous source profiles have been collected; however, there is often wide disparity among source profiles for particular source types, for example, biomass burning. It is critical that efforts be made to standardize source test procedures and the analytical methods used to determine the chemical and/or physical composition of the collected material. Continued efforts also are needed to collect source profiles for a greater number of sources (e.g., motor vehicles under common driving patters and a larger range of vehicle types) and for sources outside of California, where many of the historically available source profiles were collected.
- Applications of continuous species-specific and physical property measurement methods have allowed, within various data analysis approaches, the integration of meteorological parameters and chemical parameters at hourly or better time resolution. Additional efforts are needed to improve this integration and refine the models to use these data efficiently.
- Continued improvements in conceptual models used to describe the accumulation of PM on urban and regional spatial scales are needed to support continued improvements in receptor- and source-oriented modeling.
- Continued efforts to refine source-oriented models are needed and these are occurring currently as the databases and input data are established. A few specific areas needing improvement have been identified and include:
    - SOA formation is too slow, which results in predicted OC concentrations that are lower than measured values.
    - Oligomerization mechanisms and more detailed oxidation chemistry, including certain aspects of heterogeneous chemistry, are needed.
    - Nucleation is not well captured in the models.
    - Initial large-scale modeling suggests, for example, biases in the OC, EC, mobile/area-source NO_x, VOC, and NH_3 inventories in the Southeast, although SO_2 emissions, as expected, are better estimated.
- Evaluating and measuring primary emissions of $PM_{2.5}$ were included in four of the Supersites Projects (Houston, Pittsburgh, New York, and Fresno). Quantifying the uncertainty in emissions estimates and actually collecting new data are critical to the successful operation of source-oriented modeling. Results from this synthesis suggest much work is still needed in quantifying primary emissions from a wide variety of sources. Initial priorities should be placed on those emissions categories that are most important in resolving key uncertainties in modeling; for example, emissions from biogenic sources and NH_3 emissions from agricultural sources.
- Goals and criteria for model performance evaluation, including identifying data required for model evaluation, need to be established at the national level, so that consistent model performance can be achieved across regions.

Atmospheric Chemistry

- To develop the most effective control strategies it is necessary to better understand which species are limiting reagents and how these species vary spatially and temporally throughout the day, daily, and monthly. Measurements and modeling efforts are needed to further this understanding.

Only recently, as a result of the Supersites Program, has sufficient data become available to model these situations over the needed time periods and for multiple regions.

- Inconsistencies exist between laboratory and field observations regarding the role of acidic aerosols in the formation of SOA. Laboratory experiments need to be conducted under ambient conditions (i.e., pollutant concentrations at ambient levels, experiments operated on time scales of regional transport—days to weeks—as opposed to a maximum of 25–30 hr). Hourly ambient data are needed to deconvolute colinearity among pollutants observed with daily average measurement data. Additional analysis of ambient data should be considered and modeled to better understand the processes and conditions affecting SOA formation when acidic aerosols are present and not present.

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